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XLII. *The Disintegration of Elements by α Particles.* By Sir E. RUTHERFORD, *F.R.S., Cavendish Professor of Experimental Physics, and* J. CHADWICK, *Ph.D., Clerk Maxwell Scholar, University of Cambridge* *.

IN a former paper † we have shown that long-range particles, which can be detected by their scintillations on a zinc-sulphide screen, are liberated from the elements boron, nitrogen, fluorine, sodium, aluminium, and phosphorus under the bombardment of α rays. The range of these particles in air was greater than that of free hydrogen nuclei set in motion by α particles. Using radium C as a source of α rays, the range of the particles varied from 40 cm. for nitrogen to 90 cm. for aluminium, while the range of free hydrogen nuclei under similar conditions was about 29 cm.

Previous experiments ‡ by one of us had indicated that the long-range particles from nitrogen were deflected in a magnetic field to the extent to be expected if they were swift hydrogen nuclei ejected from the nitrogen nucleus by the impinging α particle. The nature of the particles from the other five elements was not tested, but it seemed very probable that the particles were in all cases H nuclei which were released at different speeds depending on the nature of

* Communicated by the Authors.

† Rutherford and Chadwick, Phil. Mag. vol. xlii. p. 809 (1921).

‡ Rutherford, Bakerian Lecture, Proc. Roy. Soc. A, vol. xcvii. p. 374 (1920).

the element and on the velocity of the incident α particle. Under the conditions of the experiment, these H nuclei could only arise from a disruption of the atomic nucleus by the action of the α particles.

Attention was also drawn to the remarkable fact that in the case of the one element examined, viz. aluminium, the particles were liberated in all directions relative to the incident α particles.

In the present paper we shall give an account of experiments to throw further light on these points and to test whether any evidence of artificial disintegration can be observed in the case of other light elements.

Magnetic Deflexion of the Particles.

In the course of this work, the microscope used for the counting of scintillations has been further improved. For the present experiments it was essential, in order to obtain a sufficient number of scintillations per minute, that the area of zinc-sulphide screen under observation should be greatly increased without diminution of the light-gathering power of the microscope system. Following the suggestion of Dr. Hartridge, a modified form of Kellner eyepiece was constructed. A planoconvex lens of about 7 cm. focal length was placed so as to render the rays of light from the objective approximately parallel, and the image so formed was viewed through an eyepiece consisting of a similar lens and an eye-lens of 4 cm. focal length. Used in conjunction with the old objective, Watson's Holoscopic of 16 mm. focal length and ·45 numerical aperture, this system gave a field of view of a little more than 6 mm. diameter. A rectangular diaphragm was placed in the eyepiece, limiting the field of view to an area 6 mm. $\times$ 4·9 mm. Our previous system had a field of view of 8·3 sq. mm. area, so that the new microscope, under similar conditions, gave about three times the number of scintillations of the old.

The precautions adopted in counting were similar to those described in our previous paper.

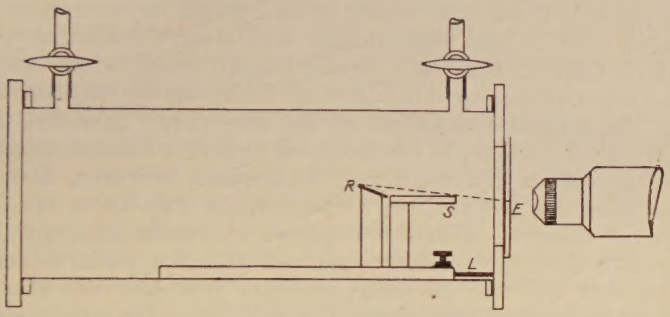
The method of measuring the magnetic deflexion of the long particles was very similar to that described by one * of us in the Bakerian Lecture of 1920. The experimental arrangement is shown in fig. 1.

The source of α rays was placed at R and was inclined at an angle of 20° to the horizontal. The lower edge was level with the face of a brass plate S which acted as a slit.

* Rutherford, *loc. cit.*

The distance from the centre of the source to the farther edge of the slit was 2·95 cm. The carrier of the source and slit was placed in a rectangular brass box between the poles of an electromagnet, the field being perpendicular to the length of the slit. A current of dry oxygen was circulated through the box during the experiment.

Fig. 1.



An extension piece L, projecting 1·7 cm. beyond the edge of the slit, was fixed to the carrier in order to increase the amount of deflexion of the particles issuing from the slit. In the end of the box was a hole 1 cm. wide and 2 cm. long covered with a sheet of mica of 3·62 cm. stopping-power. The ZnS screen was fixed on the face of the box, leaving a slot of 1 mm. depth in which absorbing screens could be inserted.

The source R was a brass disk of 1·2 cm. diameter coated with the active deposit of radium. Its initial γ-ray activity was usually equivalent to about 40 mgm. Ra.

The material, the particles from which were to be investigated, was laid directly on the source if in the form of foil, or if in the form of powder dusted over its face.

The experiment consists in obtaining an estimate of the deflexion of the particles falling on the screen by observing the effect of a magnetic field on the number of scintillations near the line E, the edge of the undeflected beam of particles. The position of the microscope was fixed in the following way:—After placing the source of α rays in position, hydrogen was passed through the box. The α rays could then strike the ZnS screen, and the edge E of the beam was clearly defined. The microscope was adjusted so that the

edge of the beam of scintillations appeared a little above a horizontal cross-wire in the eyepiece of the microscope, marking the centre of the field of view.

When the magnetic field was applied in such a way as to bend the α particles upwards (called the positive direction of the field), the edge of the beam is deflected downwards in the field of the microscope and the scintillations appear only in the lower half. When the field was applied in the opposite direction (negative field), the edge of the beam moved upwards in the field of view. The strength of the magnetic fields used in the experiments was always such that the whole field of view was covered with scintillations when the negative magnetic field was applied. In the experiments on the magnetic deflexion of the long-range particles, the number of particles is far too small to give a band of scintillations with a definite edge. It is clear, however, that if the particles are positively charged, the number of scintillations observed with the negative magnetic field will be greater than the number observed with the positive field, and that the ratio of these numbers will give a measure of the amount of deflexion of the particles. By determining this ratio for the long-range particles and comparing it with that for projected H particles of known velocity, we can obtain an approximate value for the magnetic deflexion of the long-range particles. The general method of the reduction of the observations is perhaps best shown by an account of the experiments on the particles from aluminium.

Experiments on Particles from Aluminium.

After fixing the position of the microscope in the way described above, an aluminium foil of 3·37 cm. stopping-power was placed over the source. Dry oxygen was passed through the box, and a mica sheet of 10 cm. stopping-power was inserted in front of the ZnS screen. The total absorption between the source and screen was then equivalent to 30 cm. of air. The scintillations observed were consequently due to long-range particles from the bombarded aluminium; the ranges of the particles under observation varied from 30 cm. to 90 cm., the average range being about 45 cm.

Counts of the numbers of scintillations observed with positive and negative fields due to an exciting current of 6 amps. were then made. The mean ratio of the numbers with a − field to those with a + field obtained from several experiments was 3·7. The observations were repeated with

a field due to an exciting current of 4 amps.; the corresponding ratio was 2·1.

When the source had decayed to a small fraction of its initial value, the aluminium foil over the source was removed and a thin sheet of paraffin wax put in its place. The mica sheet in front of the ZnS screen was replaced by a sheet of 3·4 cm. stopping-power, making the total absorption equivalent to 16 cm. of air. The scintillations observed on the screen were now due to H particles ejected from the paraffin wax of ranges between 16 cm. and 29 cm., the average range being about 22 cm. The ratio of the numbers of scintillations for − and + fields was determined for an exciting current of 4 amps. and found to be 3·2.

It appears from these results that the long-range particles from aluminium of average range 45 cm. were less deflected by the same magnetic field than H particles of average range 22 cm.; and that in the magnetic field due to a current of 6 amps., which was 1·34 times the intensity of the field due to 4 amps., they were more deflected than were the H particles in the latter field. To a first approximation we may say that the value of mv/e for particles from aluminium of range 45 cm. is 1·23 times greater than that for H particles of range 22 cm. This result is clearly consistent with the view that the particles from aluminium are H nuclei moving with high velocity; for, assuming that the range of the H particle is proportional to the cube of its velocity, the velocity of a particle of range 45 cm. is 1·27 times that of a particle of 22 cm. range.

These experiments show, therefore, that the particles from aluminium carry a positive charge and are deflected in a magnetic field to the degree to be anticipated if they are hydrogen nuclei moving with a velocity estimated from their range. While there can be little doubt that the particles are hydrogen nuclei, it is very difficult to prove this point definitely without an actual determination of the velocity and value of e/m of the particles. Our knowledge of the relation between the range and velocity of complex charged particles is too indefinite for purposes of calculation. On the other hand, if we assume, as seems *a priori* probable, that the ejected particle is the free nucleus of an atom, it is possible to show with some confidence that only a particle of mass 1 and charge 1 can fit the experimental results.

Additional evidence as to the value of mv/e of the particles from aluminium was obtained by comparing their magnetic deflexion with that of the α particles of 8·6 cm. range emitted by thorium C. In this experiment the source R was a very

weak source of the thorium active deposit obtained by exposing a disk to thorium emanation. Hydrogen was passed through the box, and sufficient absorbing screens were inserted in front of the ZnS screen to cut out the 5 cm. α particles of thorium C. The numbers of α particles falling on the screen for − and + fields due to an exciting current of 6 amps. were counted, and the ratio of these numbers was found to be 2·4. Comparing this ratio with those found for the long-range particles, we see that the value of mv/e for the latter is about 0·8 of that for α particles of 8·6 cm. range, *i. e.* about $3{\cdot}4 \times 10^5$ e.m. units. The calculated value, assuming that the particles are H nuclei and that their velocity is proportional to the cube root of the range, is about $3{\cdot}7 \times 10^5$ e.m. units. Considering the difficulty of the experiments, the agreement is satisfactory.

Experiments on Phosphorus and Fluorine.

Measurements similar to the above have also been made on phosphorus and fluorine.

In the case of phosphorus, a thin layer of red phosphorus was dusted over the face of the source. The total absorption in the path of the particles was about 35 cm.; the range of the particles under observation varied therefore from 35 cm. to the maximum range of 65 cm., the average being about 45 cm. The ratio of the numbers of scintillations for — and + fields due to current of 4 amps. was 2·0.

In the case of fluorine finely powdered calcium fluoride was dusted over the source. Previous experiments have shown that no long-range particles are emitted from calcium. The total absorption in the path of the particles was about 30 cm. The maximum range of the particles from fluorine is approximately 65 cm., and the average range of the particles falling on the screen was around 40 cm. The ratio of the numbers of particles observed for − and + fields due to an exciting current of 4 amperes was 2·5.

It is clear from these results that, within the error of experiment, the particles liberated from phosphorus and from fluorine are bent in a magnetic field to approximately the same extent as the particles from aluminium. We may conclude, therefore, that these particles also are H nuclei moving with high speed.

We have not examined the particles from boron and sodium in this way, but there seems no reason to doubt that they also consist of H nuclei.

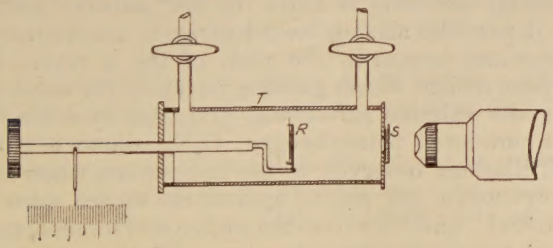
The Ranges of the H *Particles.*

In the experiments described in our previous paper only two elements, nitrogen and aluminium, were investigated in any detail. The other elements were examined in a qualitative manner, but it was shown that the ranges of the liberated H particles were in every case greater than 40 cm. of air. The ranges of the particles from these elements—viz. boron, fluorine, sodium, and phosphorus—have now been determined more accurately.

Attention has been drawn to the remarkable fact that the H particles liberated from aluminium appeared not only in the direction of the incident α particles but also in the reverse direction. The number of particles emitted in the backward direction was of the same order of magnitude as for the forward, but the maximum range in the backward direction was smaller, being 67 cm. as against the 90 cm. range of the forward particles, for α particles of 7 cm. range. Some experiments with nitrogen showed that the number of H particles emitted in the backward direction was very small at absorptions of more than 18 cm. of air.

We have repeated these experiments and extended them to include the other elements boron, fluorine, sodium, and phosphorus, with the result that we find that in every case the H particles emitted on disintegration of the nucleus escape in all directions, the maximum range in the backward being less than in the forward direction.

Fig. 2.



The experimental arrangement for the measurement of the ranges of the forward particles was the same as that described in our previous paper. The apparatus used in the investigation of the particles in the reverse direction differed from this in the arrangement of the source, and is shown in the diagram (fig. 2).

The source of α particles was carried on a rod passing with a sliding fit through a stopper which fitted tightly into the

brass tube T of 3 cm. diameter. The end of this tube was provided with a hole 7·5 mm. in diameter, closed by a silver foil of 3·75 cm. air equivalent. The zinc sulphide screen S was fixed on the face of the vessel leaving a slot in which absorbing screens could be inserted. The apparatus was placed between the poles of an electromagnet to reduce the luminosity produced in the screen by the β rays.

The source R was a silver foil of 4·15 cm. stopping-power coated on one side only with the active deposit of radium. Its initial γ-ray activity was in most experiments equivalent to about 30 mg. Ra. The inactive side of the silver foil faced towards the ZnS screen. The distance of the source from the screen was generally about 3·5 cm., but could be varied, and its position read off on a scale. The elements to be examined could in most cases only be obtained in the combined state. The powdered compound was heated in vacuo, and a film prepared by dusting on to a foil smeared with alcohol. The screen thus prepared was placed immediately behind the source. As in our previous experiments, a stream of dry oxygen was circulated through the apparatus.

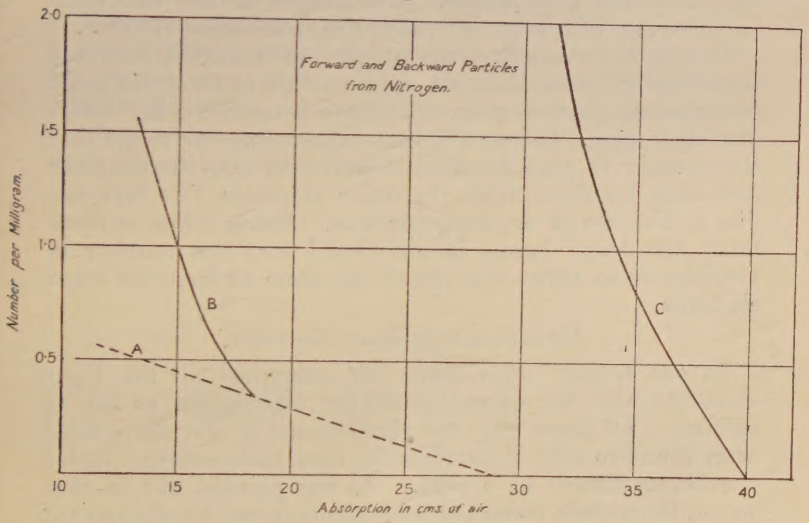
In all cases, except that of nitrogen, the maximum range of the particles emitted in the backward direction was greater than the range of free hydrogen particles, so that no complication arises from the presence of hydrogen in the silver foils or other materials in the path of the α particles.

In the case of nitrogen, however, as our previous experiments had shown, the range of the backward particles is much less than that of free hydrogen particles, and it was consequently necessary to allow for the "natural" effect, *i. e.* for the H particles arising from hydrogen contamination of the source and screens in the path of the α rays. It was found inconvenient to use gaseous nitrogen for these experiments, and a suitable screen was prepared by sifting a thin layer of powdered paracyanogen, C_xN_x, on to a gold foil. The scintillations observed on the ZnS screen when the film of paracyanogen was placed against the source were due to the "natural" particles from the source and screens, together with those which came from the nitrogen in the paracyanogen. On taking away the film of C_xN_x the natural particles alone were counted. In some experiments a film of paraffin wax was placed against the source. The natural effect remained the same, showing that even if the film of paracyanogen contained a large amount of hydrogen the number of free H particles scattered to the ZnS screen by the walls of the vessel was negligible.

Figure 3 shows the type of results obtained in these

experiments. The ordinates represent the number of scintillations observed per minute per milligram of activity of radium C, measured by γ rays; the abscissæ, the stopping power for α rays of the absorbing screens, expressed in terms of centimetres of air. The dotted curve A gives the natural effect observed when the screen of paracyanogen was absent or replaced by a film of paraffin wax; the full curve B the effect when present. The difference of these curves therefore represents the effect due to the nitrogen in the paracyanogen. It will be seen that the maximum range of the

Fig. 3.



backward particles from nitrogen is about 18 cm. Curve C is the absorption curve for the particles emitted by nitrogen in the forward direction.

In the following table are given the maximum ranges of the particles liberated from the elements which show the disintegration effect, for both forward and backward directions.

Element.	Forward range. cm.	Backward range. cm.
Boron	58	38
Nitrogen	40	18
Fluorine	65	48
Sodium	58	36
Aluminium	90	67
Phosphorus	65	49

It should be pointed out that the ranges of the forward particles from boron, fluorine, sodium, and phosphorus may be subject to considerable error, owing to the use of a film of powder as the bombarded material. The particles of maximum range are produced on the surface of the grains of powder, and therefore to find the true range the size and air equivalent of the grains of powder must be known. For the ranges given above it has been assumed that the grains were uniform in size and an average value of the air equivalent of the film of powder has been calculated from its weight per sq. cm. The ranges so determined are obviously somewhat less than the true ranges. The ranges of the backward particles are, of course, not subject to this source of error.

It was observed that the number of particles liberated from the different elements appeared all to be of the same order of magnitude when allowance is made for the difference in range. In our original experiments we found that the number of particles from boron was somewhat smaller than the numbers from the other elements, but this was due to the use of an irregular film. Using a film of more finely powdered boron it was found that the number of particles from boron was about the same as from the other elements.

Examination of other Elements.

In our former experiments we examined all the light elements, with the exception of the rare gases, as far as calcium. Of these only the six elements of the above table were found to emit H particles in detectable amount under the bombardment of α rays. As was pointed out in that paper, the atomic masses of these elements can be represented by $4n+a$ where n is a whole number, a result which receives a simple explanation on the assumption that the nuclei of these elements are composed of helium nuclei of mass 4 and hydrogen nuclei. On the other hand, some of the light elements which gave no detectable number of H particles also had atomic masses given by $4n+a$. It was thus a point of great importance to repeat the examination of these elements with the improved microscope, and to search, if possible, for the emission of particles of shorter range than free H nuclei. In some cases it was only possible, on account of hydrogen contamination of the materials, to observe at absorptions greater than 30 cm. of air, while in others the observations were carried well within this range.

Lithium was examined as oxide and as metal, a thin sheet of the latter being obtained by pressing molten lithium

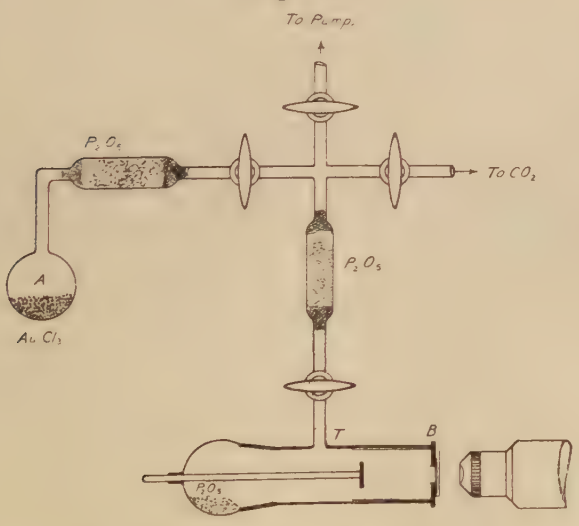
between two steel plates in an atmosphere of carbon dioxide. No evidence was found of any particles of range greater than 30 cm. Owing to hydrogen contamination of the Li and Li_2O the observations at smaller ranges were not decisive. Observations in the backward direction revealed no detectable number of particles of range greater than 14 cm.

Beryllium was examined as the powdered oxide, and there was again no evidence of the emission of particles of longer range than 30 cm. in the forward direction or 15 cm. in the backward.

Magnesium was examined with a sheet of the metal and also with a screen of powdered magnesium. There was no evidence of long-range particles.

For silicon a screen of powdered silicon and a thin sheet of quartz were used. With the sheet of quartz it was possible to make observations in the forward direction at absorptions as low as 17 cm. The scintillations observed were due entirely to the natural H particles.

Fig. 4.



Chlorine had been previously examined in the form of various chlorides. These observations were repeated, and the results confirmed the conclusion that particles of greater range than 30 cm. were not liberated in any detectable amount. In order to pursue the observations within the range of free H particles a special series of experiments was

carried out. A glass apparatus, similar in design to the standard apparatus, was used. The details will be clear from the diagram (fig. 4).

In order to avoid the bombardment of the glass walls and consequent liberation of H particles the inside of the tube was lined with platinum foil. The surfaces of the brass plate B and of the rod carrying the source were protected from the action of the chlorine by a coating of hard pitch. The stopcocks and ground-joint were lubricated with a brominated grease. The source of α rays was a platinum foil coated with radium active deposit. Pure dry chlorine was prepared by heating gold chloride, $AuCl_3$, contained in the tube A, and was passed over P_2O_5 before entering the vessel T. As an additional precaution a little P_2O_5 was placed in the vessel itself.

When the source was placed in position the air was removed by pumping and washing with dry carbon dioxide. Carbon dioxide was then let in to atmospheric pressure and the natural H particles were counted at absorptions varying from 16 cm. to 30 cm. The carbon dioxide was then replaced by chlorine, and the scintillations at similar absorptions were observed. The chlorine was then allowed to be reabsorbed by the gold chloride and carbon dioxide let in again. In this way counts on the chlorine were included between counts of the natural particles, and any traces of adventitious hydrogen could be allowed for. The results showed no evidence of the liberation of H particles from chlorine in the range examined, *i. e.* at absorptions more than 16 cm. of air.

Discussion of Results.

For convenience of discussion the atomic numbers and the masses of the isotopes of the elements from hydrogen to potassium are given in the following table. Of these elements aluminium is the only one which has not yet been examined for isotopes, but it appears likely that it is a pure element of atomic mass 27. With the exception of helium, neon, and argon, all the elements in the table have been tested to see whether H nuclei are ejected by the action of α particles. The six active elements, as they may be termed for convenience, are underlined.

TABLE I.

Element.	Atomic Number.	Atomic Masses.	Element.	Atomic Number.	Atomic Masses.
H	1	1·008	Na	11	23
He	2	4·00	Mg	12	24, 25, 26
Li	3	6, 7	Al	13	27
Be	4	9	Si	14	28. 29
B	5	10, 11	P	15	31
C	6	12	S	16	32
N	7	14	Cl	17	35, 37
O	8	16	A	18	36, 40
Fl	9	19	K	19	39, 41
Ne	10	20, 22			

An examination of the table shows that the active elements may be classified in different ways:—

(1) Active elements are odd-numbered elements in a regular sequence of numbers, viz., 5, 7, 9, 11, 13, 15.

(2) The atomic masses of the active elements are given by $4n+a$ where n is a whole number; $a=3$ for all the elements except nitrogen, for which it is 2.

(3) With the exception of boron, which has two isotopes (10, 11), the active elements are all pure elements.

We have seen that no evidence has been obtained that the preceding element lithium (3), and the succeeding elements, chlorine (17) and potassium (19), show any trace of activity under α-ray bombardment, although they are odd-numbered elements and the masses of their isotopes are given by $4n+a$. Magnesium and silicon, which are even-numbered, but which contain isotopes of mass $4n+1$ or $4n+2$, show no sign of activity.

There thus appears to be no obvious general relation which differentiates active from inactive elements. The activity starts sharply with boron and ends abruptly with phosphorus. It is a very unexpected observation that neither lithium nor chlorine shows any certain evidence of activity in the emission of either long-range or short-range particles. It is of interest to consider whether any deduction can be made as to the structure of these nuclei in the light of these experimental facts.

In our previous paper it was pointed out that the H nuclei

liberated from the active elements probably existed as satellites circulating in orbits round the main nucleus. In the case of an effective collision of an α particle with such a nucleus, part of the momentum of the α particle is communicated to the central nucleus, but the satellite is sufficiently distant from the latter to acquire enough momentum and energy to escape from the system. It was shown that such a point of view offers a general explanation of the variation of the velocity of the expelled H nuclei with the speed of the α particle and also of the escape of the H nuclei in all directions. The chance of ejecting an H satellite at high speed from a nucleus is much smaller (for nitrogen, for example, about 1/20) than the chance of setting a free H nucleus in correspondingly rapid motion. It appears therefore that the release of the satellite only takes place under certain restricted conditions of the collision of the α particle with the nucleus. If the H satellites were present in lithium and chlorine and were very lightly bound to the nucleus, it is to be anticipated that the number released by the α rays would be of the same order of magnitude as if the H nuclei were free. As this is found not to be the case, we may conclude that neither lithium nor chlorine has any lightly bound satellites in its nuclear structure. The complete absence of long-range particles from these elements shows that the H satellites, if they are present at all, are strongly bound to the main nucleus. If, for example, the satellite revolves very close to the nucleus, the α particle may only be able to give such a small part of its momentum to the satellite that it is unable to release it from the system. It does not, however, seem likely that the forces binding a satellite would vary greatly in passing from phosphorus to chlorine. It seems more probable that the general structure of the chlorine nucleus differs in some marked way from that of the group of active elements. The H nuclei may perhaps be definitely incorporated into the main nuclear system, so that the α particle has no chance of concentrating its energy upon a single unit of the nuclear structure. In a similar way it seems probable that lithium must differ widely in structure from the succeeding element boron. The facts brought to light in these experiments indicate that the nuclei even of light elements are very complex systems and illustrate how difficult it will be to find any simple and general rule to account for the variation in structure of successive elements.

It has been pointed out that, with the exception of the first

element boron, all the active elements are "pure" elements, *i. e.*, have no isotopes. This may be of some significance in differentiating between the structure of active and inactive elements. The absence of isotopes indicates that, as regards mass, there is only a narrow range of stability of the nucleus for a given nuclear charge; the addition or subtraction of an equal number of H nuclei and electrons leads presumably to an instability of the nuclear system. In the case of lithium and of chlorine, which form isotopes, the forces binding the nuclei together may consequently be very different from those in the case of the pure active elements. If there is any significance in this point of view, it would indicate that H satellites are only present in pure odd-numbered elements; but, as we have seen, boron is an exception to this rule.

In comparing the phenomena shown by the six active elements, it seems at once clear that nitrogen occupies an exceptional position in the group. Not only is the range of the expelled H nuclei the smallest of all the group, but the ratio of the ranges in the two directions is markedly different from those shown by the other elements. It is natural to connect this anomalous behaviour with the fact that the mass of the nitrogen nucleus is given by $4n+2$, while the rest of the group are of the class $4n+3$. The slower speed of ejection of the particles from nitrogen at first sight suggests that the H satellite is more lightly bound than in the case of the other elements. This suggestion is, however, not borne out by calculation of the distribution of momentum among the three bodies involved in the collision, viz., the α particle, the H satellite, and the residual nucleus. In our previous paper, we showed that the distribution of momentum could be calculated on certain assumptions from the observations of the ranges of the expelled nuclei in the forward and reverse directions of the α particle. It was supposed that the law of conservation of momentum holds, and that the sum of the energies of the H particle and the residual nucleus was the same whether the H particle was liberated in the forward or backward direction. It follows from these assumptions that the relative velocity of the H nucleus and the residual nucleus is the same in the two cases. The results of this calculation for the group of active elements are collected in the following table (Table II.).

TABLE II.

Distribution of Momentum.

Element.	H particle. Forward.	H particle. Backward.	Residual Nucleus. Forward.	Residual Nucleus. Backward.	α particle.	Gain in Energy
Boron	2·02 V	−1·75 V	−·54 V	3·23 V	2·52 V	42 %
Nitrogen	1·78 V	−1·32 V	1·44 V	4·54 V	·78 V	−13 %
Fluorine	2·10 V	−1·89 V	−·10 V	3·89 V	2·00 V	35 %
Sodium.....	2·02 V	−1·72 V	1·42 V	5·16 V	·56 V	6 %
Aluminium ...	2·34 V	−2·11 V	·78 V	5·23 V	·88 V	42 %
Phosphorus ...	2·10 V	−1·89 V	1·14 V	5·13 V	·76 V	15 %

The momenta are expressed in terms of the initial velocity V of the α particle. The initial momentum of the α particle, and consequently the sum of the momenta of the three bodies after collision, is therefore 4V. Momenta in the direction of the incident α particle are taken as positive, momenta in the opposite direction as negative. The percentage energy, gained from the nucleus as a result of the disintegration, is given in the last column, in terms of the initial energy of the α particle.

It will be seen that in the case of nitrogen a considerable part of the momentum of the α particle is communicated to the main nucleus, a much greater part than in the cases of the adjacent elements boron and fluorine. This indicates that the H satellite of nitrogen is in relatively close proximity to the main nucleus. It will also be noted that while for the other elements there is a gain of energy from the disruption varying from 6 per cent. for sodium to 42 per cent. for boron and aluminium, for nitrogen there is a loss of energy of 13 per cent.

It is apparent from the above table that the distribution of momentum among the three bodies varies considerably for the different elements, but, in the absence of any definite evidence of the validity of the theory on which the calculations are based, it seems inadvisable to discuss these differences in any detail at the present stage.

Cavendish Laboratory,
June 20, 1922.

XLIII. *The Distribution of Electrons around the Nucleus in the Sodium and Chlorine Atoms.* *By* W. Lawrence Bragg, *M.A., F.R.S., Langworthy Professor of Physics, The University of Manchester*: R. W. James, *M.A., Senior Lecturer in Physics, The University of Manchester*; *and* C. H. Bosanquet, *M.A., Balliol College, Oxford* *.

1. In two recent papers † in the Philosophical Magazine the authors have published the results of measurements made on the intensity of reflexion of X-rays by rock-salt. The mathematical formula for the intensity of reflexion, as calculated by Darwin ‡, involves as one of its factors the amount of radiant energy scattered in various directions by a single atom when X-rays of given amplitude fall upon it. The other factors in the formula can be evaluated. By measuring the intensity of reflexion experimentally we can therefore obtain an absolute measurement of the amplitude of the wave, scattered by a single atom, in terms of the amplitude of the incident radiation.

This measurement is of considerable interest, because it may throw some light on the distribution of the electrons around the nucleus of the atom. We regard the wave scattered by the atom, as a whole, as the resultant of a number of waves, each scattered independently by the electrons in the atom. A formula first evaluated by J. J. Thomson is used in order to calculate the amplitude of the wave scattered by a single electron. If an incident beam of plane polarized X-rays consists of waves of amplitude A, then the amplitude A′ at a distance R from the electron in a plane containing the direction of the incident radiation, and at right angles to the electric displacement, is given by

$$\frac{A'}{A} = \frac{1}{R}\frac{e^2}{mc^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here e and m are the charge and mass of the electron in electromagnetic units, and c is the velocity of light.

What we measure experimentally is the resultant amplitude of the wave-train scattered in various directions by a number Z of electrons in the atom. If all the electrons were

* Communicated by the Authors.

† Phil. Mag. vol. xli. March 1921; vol. xlii. July 1921.

‡ C. G. Darwin, Phil. Mag. vol. xxvii. pp. 315-675 (Feb. and April 1914).

concentrated in a region whose dimensions were small compared with the wave-length of the rays, then the resultant amplitude would be equal to $\frac{Z}{R}\frac{e^2}{mc^2}$, since the scattered wavelets would be in phase with each other in all directions. It is found experimentally that the measured amplitude tends to a value which is in agreement with the formula at small angles of scattering, but that at greater angles it falls to a very much smaller value. This is to be accounted for by the action of interference between the waves scattered by the electrons in an atom, which are distributed throughout a region whose dimensions are large compared with the X-ray wave-length.

It is an easy matter to calculate the average amplitude scattered in any direction by a given distribution of electrons around the nucleus. Here we are attempting to solve the reverse of this problem. The experimental results tell the amplitude of the wave scattered by the sodium and chlorine atoms through angles between 10° and 60°. We wish to use these results in order to get some idea of the manner in which the electrons are distributed.

2. In addition to Darwin's original mathematical treatment, the question of the effect on X-ray reflexion of the distribution of electrons around the atom has been dealt with by W. H. Bragg *, A. H. Compton †, and P. Debye and P. Scherrer ‡.

W. H. Bragg considered the interpretation of the diminution in the intensities of reflexion by a crystal as the glancing angle is increased, due allowance being made for the arrangement of the atoms. He concluded that "an ample explanation of the rapid diminution of intensities is to be found in the highly probable hypothesis that the scattering power of the atom is not localized at one central point in each, but is distributed through the volume of the atom." He did not regard the experimental data then available as sufficient to justify making an estimate of the distribution of the electrons. These data indicated that the intensity of reflexion fell off roughly as $\frac{1}{\sin^2\theta}$ (θ being the glancing angle), and he showed that a density of distribution of the electrons could be postulated which

* W. H. Bragg, Phil. Trans. Roy. Soc. Series A, vol. ccxv. pp. 253–274, July 1915.

† A. H. Compton, Phys. Rev. vol. ix. no. 1, Jan. 1917.

‡ P. Debye and P. Scherrer, *Phys. Zeit.* pp. 474–483, July 1918.

accounted for this law, just as an illustration of the application of the principle involved in considering spatial distribution.

A. H. Compton used the experimental results obtained by W. H. Bragg in order to calculate the electron distribution. W. H. Bragg showed that the intensity of reflexion is a function of the angle of reflexion alone, when allowance has been made for the arrangement of the atoms in the crystal, and he determined the *relative* intensity of reflexion by a number of planes in rock-salt and calcite. Compton calculated from these values the relative amplitudes of the waves scattered by the atoms in different directions, by means of the reflexion formula of Darwin, and proceeded to test various arrangements of electrons in order to find one which gave a scattering curve agreeing with that found experimentally. He supposed that the electrons were rotating in rings, governed by Bohr quantum relationships In sodium, for example, he placed four electrons on an inner ring, six on the next ring, and a single valency electron on an outer ring. In chlorine the rings contained four, six, and seven electrons respectively. Compton found that these atomic models gave a fair agreement with W. H. Bragg's results.

Debye and Scherrer came to the same conclusion as to the significance of intensities as regards electron distribution which was implied in W. H. Bragg's work and stated more fully by Compton. They considered two interesting cases. The first was that of the lithium fluoride crystal. They compared the intensity of reflexion by planes where the fluorine and lithium atoms reflected waves in phase with each other, with that by planes where these atoms acted in opposition to each other. The relative amplitudes at any angle for such planes may be expressed by the ratio $\frac{F+Li}{F-Li}$, where F and Li are the amplitudes contributed by the fluorine and lithium atoms respectively. Their figures indicated that the limiting values of $\frac{F+Li}{F-Li}$ at zero angle of scattering is 1·5, signifying that a valency electron has passed from the lithium to the fluorine atom $\left(\frac{10+2}{10-2}=1{\cdot}5\right)$.

Their intensities of reflexion were measured by the darkening of a photographic plate in the powder method of analysis which these authors initiated. In view of the

difficulties of estimating intensities in this way, of the few points which they obtained on the curve for the $\frac{F+Li}{F-Li}$ ratio, of the difficulties in interpreting intensities which we have discussed in our papers, and of the large extrapolation which they had to make in order to get the limiting value of $\frac{F+Li}{F-Li}$, we feel that their results cannot be regarded as proving that the transference of the valency electron has taken place. The fact of the transference is supported by much indirect evidence, and their conclusion is probably correct.

Debye and Scherrer also compared the intensities reflected by various planes of the diamond, and concluded that the electrons in the carbon atoms were contained within a sphere of diameter 0·43 Å, assuming a uniform distribution throughout this sphere.

In all the above cases, the results were obtained by comparing the relative intensities of reflexion by various faces. The results which we have obtained, and which will be used to calculate the distribution of electrons in sodium and chlorine, are, on the other hand, absolute determinations. The intensity of reflexion was compared in each case with the strength of the primary beam of X-rays, so that the absolute efficiency of the atom as a scattering agent could be deduced.

In a paper on "The Reflection Coefficient of Monochromatic X Rays from Rock Salt and Calcite"*, Compton made comparisons of the incident and reflected beam, for the first order reflexion from cleavage faces of these crystals. He obtained results for rock-salt which were rather less than those which we afterwards obtained for a ground face, but he noted that the effect was increased by grinding the face. In our notation the results were

$$\left.\begin{array}{ll} \text{Compton} & \dfrac{E\omega}{I} = \cdot00044 \pm \cdot00002 \\ \text{B. J. and B.} & \dfrac{E\omega}{I} = \cdot00055 \end{array}\right\} \text{NaCl (100).}$$

As Compton surmised, and as we have found experimentally, this figure for the efficiency of reflexion has to be modified considerably to allow for the extinction factor. The difference

* A. H. Compton, Phys. Rev. vol. x. p. 95, July 1917.

between his results and ours is accounted for by the extinction or increased absorption of the rays at the reflecting angle. Compton pointed out that the reflexion factor was of the order to be expected from Darwin's formula, but did not use the value he obtained to solve the electron-distribution problem.

3. For the sake of convenience of reference, the formula which forms the basis of all the calculations is quoted below. Let the intensity I_0 of a beam of homogeneous X-rays, at a given point, be defined as the total energy of radiation falling per second on an area of one square centimetre at right angles to the direction of the beam. If a crystal element of volume dV, supposed to be so small that absorption of the rays by the crystal is inappreciable, be placed so that it is bathed by the X-rays, and if it is turned with angular velocity ω through the angle at which some plane in it reflects the X-rays about an axis parallel to that plane, the theoretical expression for the total quantity of energy of radiation E reflected states that

$$\frac{E\omega}{I_0} = \frac{N^2\lambda^3}{\sin 2\theta} F^2 \cdot \frac{e^4}{m^2c^4} \frac{1+\cos^2 2\theta}{2} e^{-B\sin^2\theta} dV \quad . \quad (2)$$
$$= Q\,dV.$$

In this expression

N = Number of diffracting units per unit volume *.
λ = Wave-length of X-rays.
θ = Glancing angle at which reflexion takes place.
e = Electronic charge.
m = Electronic mass.
c = Velocity of light.

The factor $e^{-B\sin^2\theta}$ (the Debye factor) represents the effect of the thermal agitation of the atoms in reducing the intensity of reflexion.

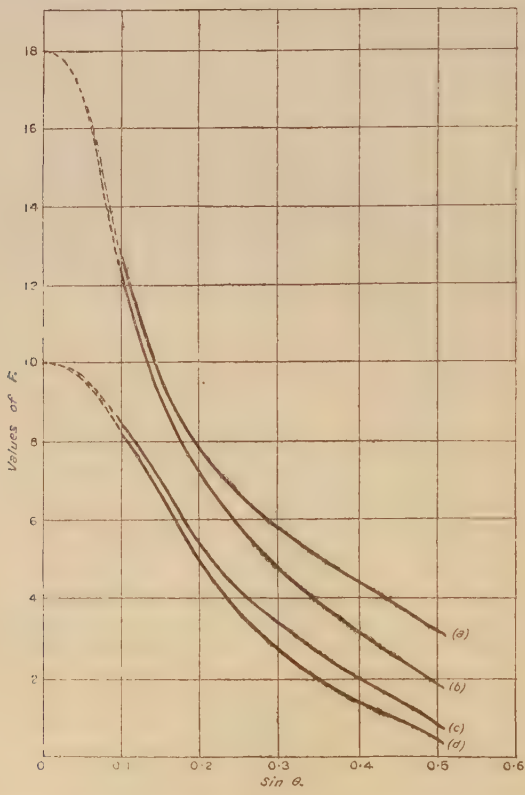
The factor F depends on the number and arrangement of the electrons in the diffracting unit. At $\theta=0$ it would have a maximum value equal to the total number of electrons in the unit, and it falls off owing to interference as θ increases.

The experimental observations have as their object the determination of Q in absolute units. In practice we cannot use a single perfect crystal so small that absorption is

* No account is taken here of the "structure factor." The diffracting units are supposed to be spherically symmetrical as regards their diffraction effects.

inappreciable. We use a large crystal consisting of numbers of such homogeneous units and deduce, from its reflecting power, the reflecting power Q per unit volume of the units of which it is composed. The assumptions made in doing this are by no means free from objections, and will be discussed later in this paper. Taking this to be justifiable, however, our experimental results yield the value of Q for rock-salt over a wide range of angles, and from them the values of F_{Cl} and F_{Na} follow directly. These values are shown in fig. 1.

Fig. 1.



(*a*) F_{Cl} corrected for Debye factor. (*c*) F_{Na} corrected for Debye factor.

(*b*) F_{Cl} uncorrected „ „ (*d*) F_{Na} uncorrected „ „

4. We must now consider more closely the significance of the factor F. The most simple case is that of a crystal containing atoms of one kind only. Parallel to any face of the

crystal we can suppose the atoms all to lie in a series of planes, successive planes being separated by a distance d. We get the nth order spectrum formed at a glancing angle by the reflexion from such a set of planes if

$$2d \sin \theta = n\lambda.$$

This spectrum represents the radiation diffracted by the atoms in a direction making an angle 2θ with the incident beam, and it is formed because in this particular direction the radiation scattered by *any* pair of atoms lying in successive planes differs in phase by $2n\pi$. Thus the amplitude of the beam scattered in this direction is the *sum* of the amplitudes scattered by all the neighbouring atoms taking part in the reflexion.

Let us consider the contribution to the reflected beam of a group of atoms lying in a reflecting plane. To obtain the amplitudes of the reflected wave, we sum up the amplitudes contributed by the electrons in all the atoms, taking due account of the fact that the electrons do not in general lie exactly in the reflecting plane and so contribute waves which are not in phase with the resultant reflected wave. By symmetry, the phase of the resultant wave will be the same as that reflected by electrons lying exactly in the geometrical plane passing through the mean positions of all these atomic centres. The phase of the wave scattered in a direction θ by an electron at a distance x from the plane differs from that of the resultant wave by an amount

$$\frac{4\pi}{\lambda} x \sin \theta.$$

We will suppose that there is in every atom an electron which is at a distance a from the centre, and that all directions of the radius joining the electron to the atomic centre are equally likely to occur in the crystal. In finding the effect of these electrons for all atoms (M in number) of the group, we may take it as equivalent to that of M electrons distributed equally over a sphere of radius a. It can easily be shown that, if x is the distance of an electron from the plane, all values of x between $+a$ and $-a$ are equally likely for both cases. Such a shell scatters a wave which is less than that scattered by M electrons in the plane in the ratio $\frac{\sin \phi}{\phi}$, where

$$\phi = \frac{4\pi}{\lambda} a \sin \theta.$$

The average contribution of the electron in each atom to the F factor is therefore $\frac{\sin\phi}{\phi}$, and not unity as it would be if the electron were at the centre of the atom.

If there are n electrons at a distance a from the centre of the atom, their contribution to the F factor would be

$$n.\frac{\sin\phi}{\phi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Any arrangement of n electrons at a distance a from the centre of the atom, provided that all orientations of the arrangement were equally probable, would make the same contribution to the F factor. For example, eight electrons arranged in a ring about the nucleus would give the same value for F as eight electrons arranged at the corners of a cube, or eight electrons rotating in orbits lying on a sphere of radius a. This illustrates the limitations of our analysis, which cannot distinguish between these cases. We can only expect to get information from our experimental results as to the average distance of the electrons from the atomic centre, and this for the average atom.

Suppose now that any atom contains a electrons at a distance r_1 from the nucleus, b at a distance r_2, c at a distance r_3 . . . n at a distance r_n, then the value of F for the average atom would be given by

$$F = a\frac{\sin\phi_1}{\phi_1} + b\frac{\sin\phi_2}{\phi_2} + c\frac{\sin\phi_3}{\phi_3} + \ldots + n\frac{\sin\phi_n}{\phi_n} \quad . \quad . \quad (4)$$

Thus, given the distribution of the electrons on a series of shells or rings, we can calculate the value of F for any value of θ. The problem we have to solve here, however, is the converse of this. We have measured the value of F for a series of values of θ, and wish to determine from the results the distribution of the electrons. We have seen above that there is no unique solution of this problem, but we can get some idea of the type of distribution which will fit the experimental curves.

In order to do this, we suppose the electrons to lie on a series of shells, of definite radii r_1, r_2, ... and determine the number of electrons a, b, c on the various shells which will give values of F corresponding to those observed experimentally. Suppose, for example, we take six shells uniformly spaced over a distance somewhat greater than

the atomic radius is expected to be. For any given value of θ we have

$$F = a\frac{\sin\phi_1}{\phi_1} + b\frac{\sin\phi_2}{\phi_2} + c\frac{\sin\phi_3}{\phi_3} + d\frac{\sin\phi_4}{\phi_4} + e\frac{\sin\phi_5}{\phi_5} + f\frac{\sin\phi_6}{\phi_6} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We chose from the experimental curve six values of θ evenly spaced over the range of values at our disposal, and for each of these values read from the curve the value of F. Since definite radii have been assumed for the shells, the values of $\frac{\sin\phi_1}{\phi_1}$, etc., can be calculated for each value of θ.

Hence, for each value of θ, we have an equation involving numerical coefficients and the quantities a, b, c, d, e, f, so that if six such equations are formed we may calculate these quantities.

If Z is the total number of electrons in the atom we have

$$Z = a+b+c+d+e+f, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and this will be taken as one of our equations (corresponding to $\theta = 0$). In calculating the results for sodium and chlorine we have assumed the atom to be ionized, and have taken $Z_{Cl} = 18$ and $Z_{Na} = 10$.

It will be evident that this method of solution is somewhat arbitrary, and that the results we get will depend on the particular radii assumed for the shells. By assuming various radii for the shells, however, and solving the simultaneous equations for the number of electrons on each, we find that the solutions agree in the number of electrons assigned to various regions of the atom.

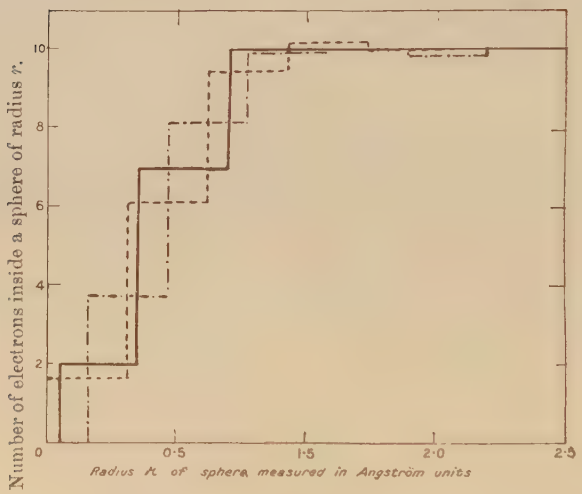
As a test of the method of analysis, a model atom was taken which was supposed to have electrons arranged as follows:—

2	on a shell	0·05 Å radius.
5	.. ..	0·35 ..
3	„ „	0·70 „

The F curve for this model was calculated. Then the simultaneous equations for the electron distribution were solved, just as if this curve had been one found experimentally. This was done for two arbitrarily chosen sets of radii, taken out to well beyond the shell at 0·70 Å.

The comparison between the two analyses (dotted curves) and the atom model we started with (continuous curve) is shown in fig. 2. The abscissæ represent the radii of the shells in Å, the ordinates the total number of electrons inside a shell of that radius. When the limits of the atomic structure are reached, the curve becomes horizontal at the value 10, corresponding to the ten electrons. The analyses not only indicate with considerable accuracy the way in

Fig. 2.



which the electron-content grows as we pass to spheres of larger radii, but also tell definitely the outer boundary of the atomic structure. Both give a number of electrons very nearly equal to zero in the shells outside 0·70 Å.

5. The F curves for sodium and chlorine can be solved in the same manner. We have expressed our results in two ways.

First, we have supposed the electrons to be grouped on shells. The numbers of electrons on each shell, and the radii of the shells, have been so adjusted as to give the best possible fit to the experimental curves. In the case of sodium it is found that a fit can be obtained with two shells, and in the case of chlorine with three shells. The

numbers of electrons on each shell, and the radii of the shells, are as follows :—

Sodium.

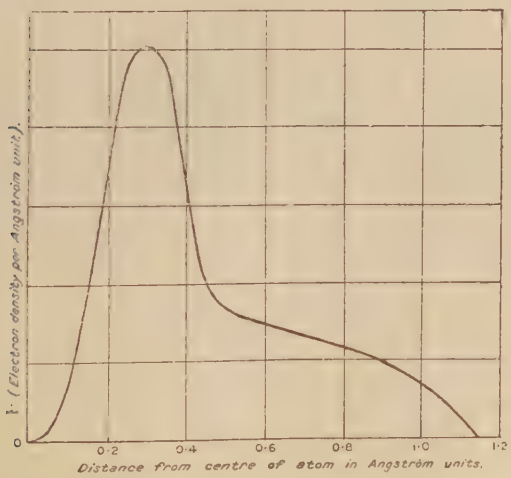
7 electrons on a shell of radius 0·29 Å.
3 „ „ „ 0·76 „

Chlorine.

10 electrons on a shell of radius 0·25 Å.
5 „ „ „ 0·86 „
3 „ „ „ 1·46 „

Secondly, we have solved the simultaneous equations for the distribution in shells with several sets of radii, and drawn a smooth curve through the points so obtained in such a way as to represent the density of distribution of the electrons as a continuous function of the distance from

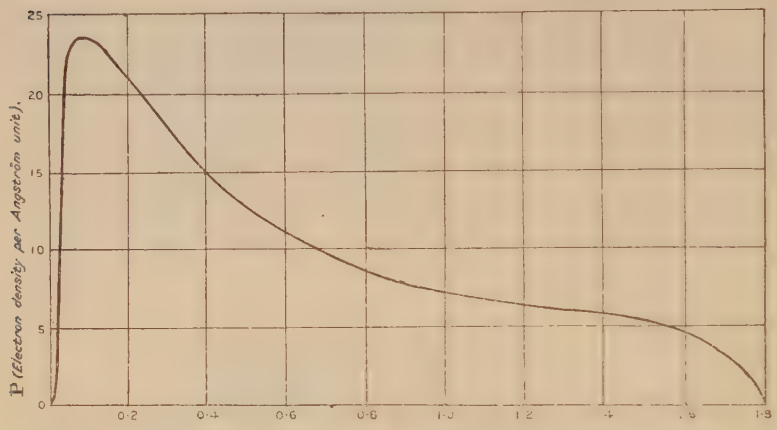
Fig. 3.



the atomic centre. The density P is so defined that Pdr is the number of electrons whose distance from the centre lies between r and $r+dr$. The curves which we obtain for sodium and for chlorine are shown in figs. 3 and 4. The

total number of electrons in the atom is represented by the area included between the curves and the axis.

Fig. 4.



Distance from centre of atom in Ångström units.

The following table shows the agreement between the F curves found experimentally and those calculated from the electron distributions:—

TABLE I.—Sodium.

	Sin θ.	0·1.	0·2.	0·3.	0·4.	0·5.
F	Observed	8·32	5·40	3·37	2·02	0·76
F	Shells { 0·29 Å, 0·76 }	8·56	5·59	3·33	2·19	0·93
F	Smooth Curve ...	8·57	5·40	3·20	1·91	1·00

TABLE II.—Chlorine.

	Sin θ.	0·1.	0·2.	0·3.	0·4.	0·5.
F	Observed	12·72	7·85	5·79	4·40	3·16
F	Shells { 0·25 Å, 0·86, 1·46 }	12·53	7·73	5·90	4·61	2·69
F	Smooth Curve ...	12·70	7·80	5·55	4·10	3·20

6. We have also made an approximate calculation of the F curve to be expected from an atom of the type proposed by Bohr *. In the ionized sodium atom containing

* Nature, cvii. p. 104 (1921).

10 electrons, two are supposed to describe circular one-quantum orbits about the nucleus, while, of the remaining eight, four describe two-quantum circular orbits and four two-quantum elliptical orbits. We have calculated the size of these orbits from the quantum relationship and the charges; this can only be done very approximately, owing to the impossibility of allowing for the interaction of the electrons. We take the following numbers:—

Radius of 1 quantum ring	0·05 Å.
,, 2 ,, ...	0·34 ,,
Semi-major axis of ellipses * ...	0·42 ,,

To get a rough idea of the diffracting power of such an atom, we suppose, first, that the orientation of the orbits is random so that the average atom has a spherical symmetry, and also that the periods of the electrons in their orbits are so large compared with the period of the X-rays that we need not consider the effect of their movements.

The calculation of the effect of the circular orbits offers no difficulties. To allow for the effect of the ellipses, the following method was used. The elliptical orbit was divided into four segments, through each of which the electron would travel in equal times. It was then assumed that, on the average, one of the four electrons describing ellipses would be in the middle of one of these segments. This gives four different values of the radius vector, corresponding in the average atom to four spherical shells of these radii.

We thus calculate the value of F for an atom having

2	electrons	on a shell of	radius	0·05 A.U.
4	,,	,,	,,	0·34 ,,
1	,,	,,	,,	0·27 ,,
1	,,	,,	,,	0·55 ,,
1	,,	,,	,,	0·70 ,,
1	,,	,,	,,	0·78 ,,

* The elliptical two-quantum orbit of a single electron about the sodium nucleus would have a semi-major axis equal to the radius of the two-quantum circle. We have used the larger value 0·42 to make some allowance for the fact that part of the orbit lies outside the inner electrons, so that the effective nuclear charge is reduced.

This gives the following figure for F_{Na}:—

Sin θ.	0·1.	0·2.	0·3.	0·4.	0·5.
F calculated	8·73	5·04	3·76	2·53	1·80
F observed	8·32	5·40	3·37	2·02	0·76

The agreement, of course, is not perfect, but one must remember that no attempt has been made to adjust the size of the orbits to fit the curve. The method of calculation too is very rough, although it must give results of the right order. The point to be noticed is that the curve is quite of the right type, and there is no doubt that an average distribution of electrons of the nature given by such an atom model could be made to fit the observed value of F quite satisfactorily.

7. The points which appear to us to be most doubtful in the above analysis of our results are the following:—

(*a*) We have assumed that each electron scatters independently, and that the amount of scattered radiation is that calculated for a free electron in space according to the classical electromagnetic theory. It is known that for very short waves this cannot be so, since the absorption of γ rays by matter is much smaller than scattering would account for, if it took place according to this law. On the other hand, the evidence points towards the truth of the classical formula in the region of wave-lengths we have used (0·615 Å).

(*b*) We have used certain formulæ (given in our previous papers, to which reference has been made) in order to calculate the quantity we have called Q in equation (2) from the observed intensity of reflexion of a large crystal. Darwin* has recently discussed the validity of these formulæ. The difficulty lies entirely in the allowance which has to be made for "extinction" in the crystal. X-rays passing through at the angle for reflexion suffer an increased absorption owing to loss of energy by reflexion.

Darwin has shown that this extinction is of two kinds, which he has called primary and secondary. If the crystalline mass is composed of a number of nearly-parallel homogeneous crystals, each so small that absorption in it is inappreciable even at the reflecting angle, then secondary extinction alone takes place. At the reflecting angle the

* Phil. Mag. vol. xliii. p. 800, May 1922.

X-rays suffer an increased absorption, because a certain fraction of the particles are so set as to reflect them and divert their energy. We made allowance for this type of extinction in our work, and Darwin concludes that our method of allowance, while not rigorously accurate mathematically, was sufficiently so for practical purposes.

Primary extinction arises in another way. The homogeneous crystals may be so large that, when set at the reflecting angle, extinction in each crystal element shelters the lower layers of that element from the X-rays. Darwin has calculated that this will take place to an appreciable extent for the (100) reflexion if the homogeneous element is more than a few thousand planes in depth. A large homogeneous element such as this does not produce an effect proportional to its volume, since its lower layers are ineffective, and a crystal composed of such elements would give too weak a reflexion. Our method of allowing for extinction will not obviate this effect.

We cannot be sure, therefore, that we have obtained a true measure of Q for the strong reflexions. The F curve may be too low at small angles. It is just here that its form is of the highest importance in making deductions as to atomic structure. Until this important question of the size of the homogeneous elements has been settled, we must regard our results as provisional.

(*c*) The allowance for the thermal agitation of the atom (the Debye factor) is only approximate; it depends on a few measurements made by W. H. Bragg in 1914. In order to see how much error is caused by our lack of knowledge of the Debye factor, we have calculated the electron distribution without making any allowance for it. The result may appear at first rather surprising; the electron distribution so calculated is almost indistinguishable from that which we found before, when allowance for the Debye factor had been made. This is so, although the factor is very appreciable for the higher orders of spectra, reducing them at ordinary temperatures to less than half the theoretical value at absolute zero. The difference which the factor makes can best be shown by comparing the radii of the shells which give the best fit with (1) the F curve deduced directly from the experimental results, (2) the F curve to which the Debye factor has been applied.

	(1). Radius (without allowance for thermal agitation).	(2). Radius (with allowance for thermal agitation).
Sodium.—Seven electrons	0·31	0·29
Three electrons	0·79	0·76
Chlorine.—Ten electrons	0·28	0·25
Seven electrons.....	0·81	0·86
Three electrons.. ...	1·46	1·46

A little consideration shows the reason for this. The form of the F curve at large angles is almost entirely decided by the arrangement of the electrons near the centre of the atom. A slight expansion of the grouping in this region causes a large falling off in the intensity of reflexion. This is shown in the analysis by the slight increase (0·02 to 0·03 Å) in the radius of the shell which gives the best fit to the uncorrected curve. The effect of the thermal agitation is to make the electron distribution appear more widely diffused : however, the average displacement of the atom from the reflecting plane owing to its thermal movements is only two or three hundredths of an Ångström unit at ordinary temperatures, and so we get very little alteration in our estimate of the electron distribution. The uncertainty as to the Debye factor, therefore, does not introduce any appreciable error in our analysis of electron distribution.

8. It is interesting to see whether any evidence can be obtained as to whether a valency electron has been transferred from one atom to the other or not. This may be put in another way : can we tell from the form of the F curves in fig. 1 whether their maxima are at 10 and 18 or at 11 and 17 respectively ? It appears impossible to do this : and, when we come to consider the problem more closely, it seems that crystal analysis must be pushed to a far greater degree of refinement before it can settle the point. If all the electrons were grouped close to the atomic centres, and if the transference of an electron meant that one electron passed from the Na group to the Cl group, then a solution along the lines of that attempted by Debye and Scherrer for LiF might be possible. The electron distributions we find extend, on the other hand, right through the volume of the crystal. The distance between Na and Cl centres is 2·81 Å, and we find electron distributions 1 Å from the centre in sodium and 1·8 Å from the centre in chlorine. If the

valency electron is transferred from the *outer region* of one atom to that of the other, it will still be in the region between the two atoms for the greater part of the time, since each atom touches six neighbours, and the difference in the diffraction effects will be exceedingly small. It is for this reason that we think Debye and Scherrer's results for LiF, which were not absolute measurements such as the above, were not adequate to decide whether the transference of a valency electron has taken place.

We have assumed that the atoms are ionized in calculating our distribution curves. If, on the other hand, we had assigned 11 electrons to sodium and 17 to chlorine, we should have obtained curves of much the same shape but with an additional electron in the outermost shells of sodium and one less in those of chlorine.

9. *Summary.*—We have attempted to analyse the distribution of electrons in the atoms of sodium and chlorine by means of our experiments on the diffraction of X-rays by these atoms. The results of the analysis are shown in figs. 3 and 4.

The principal source of error in our conclusions appears to be our ignorance as to the part played by "extinction" in affecting the intensity of X-ray spectra. The distributions of the electrons are deduced from the F curves (fig. 1). The most important parts of these curves are the initial regions at small angles, for errors made in absolute values in this region alter very considerably the deductions as to electron distribution. The exact form of the curve at large angles is of much less interest. Now, it is in this initial region, corresponding to strong reflexions such as (100), (110), (222), that extinction is so uncertain a factor. Until the question of extinction is satisfactorily dealt with, the results cannot be regarded as soundly established.

If our results are even approximately correct, they prove an important point. There cannot be, either in sodium or chlorine, an outer "shell" containing a group of eight electrons, or eight electrons describing orbits lying on an outer sphere. Such an arrangement would give a diffraction curve which could not be reconciled with the experimental results. Eight electrons revolving in circular orbits of the same radius would give the same diffraction curve as eight electrons on a spherical shell, and are equally inadmissible. On the other hand, it does seem possible that a combination of circular and elliptical orbits will give F curves agreeing with the observations.

XLIV. *On the Partition of Energy.* *By* C. G. Darwin, *M.A.*, *F.R.S.*, *Fellow and Lecturer in Christ's College, Camb.*, *and* R. H. Fowler, *M.A.*, *Fellow and Lecturer in Trinity College, Camb.**

§ 1. *Introduction.*

An important branch of atomic theory is the study of the way in which energy is partitioned among an assembly of a large number of systems—molecules, Planck vibrators, etc. This study is based on the use of the principles of probability which show that one type of arrangement is much more common than any other. The most usual method is to obtain an expression for the probability of any state described statistically and then to make this probability a maximum. This always involves a use of Stirling's approximation for factorials, which in many cases is illegitimate at first sight, and though it is possible to justify it subsequently, this justification is quite troublesome. It is also usually required to find the relation of the partition to the temperature rather than to the total energy of the assembly, and this is done by means of Boltzmann's theorem relating entropy to probability—a process entailing the same unjustified approximations.

The object of the present paper is to show that these calculations can all be much simplified by examining the average state of the assembly instead of its most probable state. The two are actually the same, but whereas the most probable state is only found by the use of Stirling's formula, the average state can be found rigorously by the help of the multinomial theorem, together with a certain not very difficult theorem in the theory of the complex variable. By this process it is possible to evaluate the average energy of any group in the assembly, and hence to deduce the relation of the partition to temperature, without the intermediary of entropy. The temperature here is measured on a special scale, which can be most simply related to the absolute scale by the use of the theorem of equipartition, and we shall also establish the same relationship directly by connecting it with the scale of a gas thermometer. Throughout the paper the analysis is presented with some attempt at rigour, but it will be found that apart from this rigour it is exceedingly easy to apply the method of calculation. Most of the results are not

* Communicated by the Authors.

new; it is the point of view and the method which, we think, differ from previous treatments

No discussion of the question of partition would be complete without consideration of its relation to thermodynamic principles. We shall leave this view of the subject to a future paper; for the increased light thrown on the statistical nature of entropy raises many interesting points which could not be discussed here properly without making the present work run to inordinate length.

§ 2. *Statistical Principles and Weight.*

Before proceeding to the problem it will be well to review, in general outline, the principles of the theory of the partition of energy, though we have nothing new to say in this connexion. We shall be concerned with collections of molecules, Planck vibrators, etc.—each individual unit will be called a *system*, and we shall call the whole collection an *assembly*. We shall be dealing mainly with assemblies composed of groups of systems, the individuals in each group being identical in nature. In order to make the problem definite it is necessary to assume that each system has a definite assignable energy, and yet can interact with the others. This requires that the time of interactions, during which there will be energy which cannot be assigned to a definite single system, is negligibly small compared with the time during which each system describes its own motion.

For such an assembly we are to calculate various average properties of its state, when it describes its natural motion according to whatever laws it may obey. There will at any rate be an energy integral, and we have therefore to calculate these averages subject to the condition of constant energy. To determine the basis on which these averages are to be calculated we are to apply the principles of probability; and the calculation of itself falls into two stages, the prior and the statistical. The prior stage aims at establishing what are the states which are to be taken as of equal probability. In the statistical stage we have simply to enumerate the states specified in the prior stage, allow for the fact that the systems are macroscopically indistinguishable, and evaluate the averages taken over these states.

It is not here our purpose to enter into a full discussion of the fundamental questions that arise in connexion with the determination of what states ought to be taken as equally

probable. It will suffice to recall that for assemblies obeying the laws of classical mechanics the theorem of Liouville shows that the elements of equal probability may be taken to be equal elements of volume in Gibbs' "phase space." It follows out of this, for example, in the case of an assembly of a number of identical systems—say simple free molecules—that the elements of equal probability can be simplified down into 6-dimensional cells $dq_1dq_2dq_3dp_1dp_2dp_3$ of equal extension, where q_1, q_2, q_3 are the coordinates, and p_1, p_2, p_3 the conjugated momenta, of a single molecule. We shall describe this by saying that the *weight* of every equal element $dq_1 \ldots dp_3$ is the same, and by a slight generalization, that the weights of unequal cells are proportional to their 6-dimensional extension. The word *weight* is here used in exactly the sense of the term *a priori probability*, as used by Bohr and others.

But when we come to the quantum theory, mechanical principles cease to hold, and we require a new basis for assigning the equally probable elements. Such a basis is provided by Ehrenfest's * Adiabatic Hypothesis and Bohr's † Correspondence Principle. These show how the theorem of Lionville is to be extended, and allow us to assign a *weight* for each quantized state of a system. It is found that we must assign an equal weight to every permissible state in each quantized degree of freedom. At first sight this is a little surprising, for it would seem natural to suppose that a vibrator which could only take energy in large units would be less likely to have a unit than one which could take it in small; but this is to confuse the two stages of the problem. It is only by the supposition of equal weights that we can obtain consistency with classical mechanics by the Correspondence Principle. It is customary ‡ in assigning a definite weight to every quantized state to give it the value h, so as to bring the result to the same dimensions as those of the element $dq\,dp$ in the classical case. But there is considerable advantage in reversing this, and taking the quantized weights as unity and the weight of the element in the phase space as $dq\,dp/h$; for if this is done, the arguments about entropy are simplified by the absence of logarithms of dimensional quantities. We shall adopt this convention here, though in

* Ehrenfest, Proc. Acad. Amst. xvi. p. 591; Phil. Mag. xxxiii. p. 500 (1917), etc.

† Bohr, "The Quantum Theory of Line Spectra," Dan. Acad. iv. p. 1 (1918).

‡ Ehrenfest & Trkal, Proc. Amst. Acad. Sc. xxiii. p. 162. See in particular p. 165 and Additional Notes, No. 1.

all our results it is immaterial—indeed, until such questions as dissociation are considered it makes no difference to adopt different conventions for different types of system. The convention has the advantage of shortening a good many formulæ and freeing them from factors which are without effect on the final results.

An exception to the above rule for assigning weights to quantized motions occurs in the case of *degenerate systems*, where there are two degrees of freedom possessing the same or commensurable frequencies. In this case there is only one quantum number, and the state of the system is partly arbitrary. Bohr * shows that the rational generalization is to assign to such a state a weight factor which can be evaluated by treating the system as the limit of a non-degenerate system, and quantizing it according to any pair of variables in which it is possible to do so. The number of the permissible states which possess the same total quantum number will give the weight of the state. A corresponding rule holds for systems degenerate in three or more degrees of freedom.

The meaning of weight can perhaps be made clearer by considering its introduction the other way round—beginning with an assembly of simple quantized systems of various frequencies. Given the energy, there is a definite number of possible states, which are fully specified by the energy assigned to each system. We then make the hypothesis that it is right to assign an equal probability to each such state in the calculation of averages. This is now the fundamental postulate. The generalization to degenerate systems goes as before, by introducing weight factors. Finally, passing over to mechanical systems, such as free molecules, we are led by an appeal to the converse of the Correspondence Principle to attach weight $dq_1 \ldots dp_3/h^3$ to each 6-dimensional cell which specifies completely the state of a single molecule.

The second, statistical, half of the problem consists in enumerating the various *complexions* possible to the assembly. By a *complexion* we mean every arrangement of the assembly, in which we are supposed to be able to distinguish the individuality of the separate systems. We count up the total number of complexions which conform to any specified statistical state of the assembly, and attach to each the appropriate weight factor. Thus the probability of this state is the ratio of the number of its weighted complexions to the

* Bohr, *loc. cit.* p. 26.

total number of all possible weighted complexions. This part of the problem depends on the nature of the particular assembly considered, and so must be treated separately in each case.

We start in § 3 with a problem which concerns not the partition of energy, but the distribution of molecules in a volume. It illustrates the method in its simplest aspect and has the advantage of being purely algebraic. Next, in § 4, we take the distribution of energy among a set of similar Planck vibrators, which is again a purely algebraic process, and then proceed in § 5 to introduce the main theme of this paper by dealing with the partition of energy between two sets of Planck vibrators of different type. This is most conveniently treated by using the complex variable, and in § 6 there is a discussion of the required theorem. The partition of itself introduces the temperature, and in § 7 the special scale is compared with the absolute. In §§ 9, 10, 11 the partition law is generalized to more complicated types of system, such as the quantized rotations of molecules. In §§ 12, 13 the method is extended so as to deal with the free motion of monatomic molecules, intermixed with vibrators. The work leads to a rather neat method of establishing the Maxwell distribution law.

§ 3. *The Distribution of Molecules in Space.*

The first example we shall take is not one of a partition of energy, but of the distribution of small molecules in a vessel. It illustrates in its simplest form the averaging process, and has the advantage of depending only on elementary algebra.

Let there be M molecules, and divide the vessel into m cells of equal or unequal volumes $v_1, v_2 \ldots v_m$, which may each be as large or as small as we like. Then

$$v_1 + v_2 + \ldots + v_m = \mathrm{V}. \quad . \quad . \quad . \quad . \quad (3{\cdot}1)$$

By well-known arguments which we need not consider, it follows that any one molecule is as likely to be in any element of volume as in any other equal one. So by a slight extension of the idea of weight we attach weights $v_1, v_2, \ldots v_m$ to the cells. To specify the statistical state we say that the first cells has a_1 molecules, the second a_2, and so on. Then

$$a_1 + a_2 + \ldots + a_m = \mathrm{M}. \quad . \quad . \quad . \quad . \quad (3{\cdot}2)$$

By the theory of permutations the number of complexions

which conform to the specification is

$$\frac{M!}{a_1!\,a_2!\ldots a_m!},$$

and each of these must be weighted with a factor

$$v_1^{a_1}v_2^{a_2}\ldots v_m^{a_m}.$$

The total number of all the weighted complexions is

$$C=\Sigma_a\frac{M!}{a_1!\,a_2!\ldots}v_1^{a_1}v_2^{a_2}\ldots,$$
$$=(v_1+v_2+\ldots)^M=V^M,$$

by the multinominal theorem. This could have been deduced at once by working direct with probabilities v_r/V instead of weights v_r, but the argument has been given in detail to illustrate the method for more complicated cases.

We next find the average value of a_r. This is given by

$$Ca_r=\Sigma_a a_r\frac{M!}{a_1!\,a_2!\ldots}v_1^{a_1}v_2^{a_2}\ldots.$$

To sum this expression we only have to cancel a_r with the first factor in $a_r!$ in the denominator, and then it is seen to be equal to

$$Mv_r(v_1+v_2+\ldots)^{M-1},$$

and so, as is implicit in our assumptions,

$$\bar{a}_r=Mv_r/V. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3{\cdot}3)$$

But we can now go further and find the range over which a_r will be likely to fluctuate. This is estimated by averaging the square of the difference of a_r from its mean value. We shall throughout this paper describe such a mean square departure as the *fluctuation* of the corresponding quantity. Thus the *fluctuation* of a_r is $(a_r-\bar{a}_r)^2$. Now

$$(a_r-\bar{a}_r)^2=a_r(a_r-1)+a_r-2a\,\bar{a}_r+\bar{a}_r^2,$$

and averaging the separate terms by the multinominal theorem, we have

$$\overline{(a_r-a_r)^2}=\frac{M(M-1)v_r^2}{V^2}+\frac{Mv_r}{V}-\frac{2Mv_r}{V}\cdot\frac{Mv_r}{V}+\left(\frac{Mv_r}{V}\right)^2$$
$$=\frac{Mv_r}{V}\left(1-\frac{v_r}{V}\right)=\bar{a}_r\left(1-\frac{a_r}{M}\right). \quad . \quad . \quad . \quad (3{\cdot}4)$$

This result represents the *fluctuation* however large or small

v_r may be. In all cases we have the result that $(a_r - \overline{a_r})^2$ is less than $\overline{a_r}$, and therefore that the average departure of a_r from $\overline{a_r}$ is of order $(\overline{a_r})^{\frac{1}{2}}$. We can also interpret this fact by saying that departures of a_r from $\overline{a_r}$ which are much greater than $(\overline{a_r})^{\frac{1}{2}}$ will be relatively rare; as M is large and $(a_r)^{\frac{1}{2}}$ small compared with a_r, this is precisely equivalent to saying that the possession of the average value of a_r is a *normal* property of the assembly in the sense used by Jeans *. We have thus a simple and *complete* proof that uniform density is a normal property of this assembly.

§ 4. *The Distribution of Energy among a Set of Planck Vibrators.*

Another case where the treatment can be almost entirely algebraic is that of the partition of energy among a set of Planck vibrators which all have the same frequency. Let ϵ be the unit of energy so that every vibrator can have any multiple of ϵ. As we saw in § 2, the weight attached to every state is to be taken as unity.

Let there be M vibrators and let there be $P\epsilon$ of energy (P is an integer) to be partitioned among them. To specify a statistical state, let a_0 be the number of vibrators with no energy, a_1 with ϵ, a_2 with 2ϵ, etc. Then we have

$$a_0 + a_1 + a_2 + a_3 + \ldots = M, \quad . \quad . \quad . \quad . \quad (4{\cdot}1)$$

$$a_1 + 2a_2 + 3a_3 + \ldots = P, \quad . \quad . \quad . \quad . \quad (4{\cdot}2)$$

and any set of a's which satisfy these equations corresponds to a possible state of the assembly. By the principles of § 2 each of the complexions will have unit weight. Now count up the number of complexions corresponding to the specification. By considering the various permutations of the vibrators, it is seen to be

$$\frac{M!}{a_0!\, a_1!\, a_2! \ldots} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4{\cdot}3)$$

We must next find C the total number of all possible complexions. Let Σ_a denote summation over all possible values of the a's which satisfy (4·1) and (4·2). Then

$$C = \Sigma_a \frac{M!}{a_0!\, a_1!\, a_2! \ldots}.$$

Consider the infinite series

$$(1 + z + z^2 + z^3 + \ldots)^M$$

* Jeans, 'Dynamical Theory of Gases,' *passim.*

expanded by the multinominal theorem. The typical term is

$$\frac{M!}{a_0!\,a_1!\,a_2!\ldots}z^{a_1+2a_2+3a_3\ldots},$$

where the a's take any values consistent with (4·1). Then if we pick out the coefficient of z^P, we have the sum of all the expressions for which the a's satisfy both (4·1) and (4·2). Observe that we may take the whole infinite series because the later terms are automatically excluded.

Now this will be the coefficient of z^P in $(1-z)^{-M}$, and so

$$C=\frac{(M+P-1)!}{(M-1)!\,P!}, \quad . \quad . \quad . \quad . \quad . \quad (4\cdot4)$$

which is the ordinary expression for the number of homogeneous products as formerly used by Planck *.

We next evaluate the average of a_r;

$$C\bar{a_r}=\Sigma_a a_r\frac{M!}{a_0!\,a_1!\,a_2!\ldots},$$

$$=M\Sigma_{a'}\frac{(M-1)!}{a_0'!\,a_1'!\,a_2'!\ldots},$$

where $\Sigma_{a'}$ denotes summation over all values satisfying

$$a_0'+a_1'+a_2'+a_3'\ldots=M-1,$$

$$a_1'+2a_2'+3a_3'\ldots=P-r.$$

The sum is thus

$$M\frac{(M+P-r-2)!}{(M-2)!\,(P-r)!},$$

and we have

$$\bar{a_r}=M(M-1)\frac{(M+P-r-2)!}{(M+P-1)!}\frac{P!}{(P-r)!}.$$

This is exact, and holds for all values of r; now r can have any value up to P and the majority of the a_r's will be zero. The ordinary method of proof applies Stirling's formula for $a_r!$ to these zero values. In the important case where both M and P are large, it will be only necessary to consider values of r which are small compared with P. Now, if r^2 is small compared with P, $P!/(P-r)!$ has the asymptotic value P^r. Using relations of this type and also disregarding the difference between M and $M-1$, we have

$$\bar{a_r}=\frac{M^2P^r}{(M+P)^{r+1}}. \quad . \quad . \quad . \quad . \quad . \quad (4\cdot5)$$

* M. Planck in the earlier editions of his book on Radiation.

The same methods give the fluctuations of a_r. For

$$\overline{(a_r-\bar{a}_r)^2}=\overline{a_r(a_r-1)}+\bar{a}_r-(\bar{a}_r)^2,$$

and a process similar to the above gives

$$\overline{a_r(a_r-1)}=\mathrm{M}(\mathrm{M}-1)\frac{(\mathrm{M}+\mathrm{P}-2r-3)!}{(\mathrm{M}-3)!\,(\mathrm{P}-2r)!}.$$

The exact expression for the fluctuation can be at once put down. When M and P are taken large the leading term cuts out, and so it is necessary to carry the approximation to the next order. If we substitute

$$\mathrm{P}!/(\mathrm{P}-r)!\sim\mathrm{P}^r-\tfrac{1}{2}r(r-1)\mathrm{P}^{r-1},$$

we find that

$$(a_r-\bar{a}_r)^2=$$
$$\bar{a}_r\left\{1-\frac{\mathrm{MP}^{r-1}}{(\mathrm{M}+\mathrm{P})^{r+2}}[2\mathrm{P}^2-(2r-1)\mathrm{MP}+r^2\mathrm{M}^2]\right\}. \quad (4{\cdot}6)$$

The formula for a_r can be put into a more familiar form by the substitution $\mathrm{P}=\mathrm{M}/(e^{\alpha}-1)$, which gives

$$\bar{a}_r=\mathrm{M}e^{-r\alpha}(1-e^{-\alpha}), \quad . \quad . \quad . \quad . \quad (4{\cdot}7)$$

and leads to a corresponding but more complicated expression for the fluctuation. Here, as we shall see later, α can be identified with the familiar $\epsilon/k\mathrm{T}$. Equation (4·6) establishes at once that the statistical state specified by (4·5) or (4·7) is a normal property of the assembly.

§ 5. *The Partition of Energy among two Sets of Planck Vibrators.*

After these preliminary examples we now apply our method to a problem which will bring out its distinctive character, that of the partition of energy in an assembly composed of different types of system. We shall consider first the simplest of such cases—an assembly consisting of a large number of Planck vibrators of two types A and B. The number of A's is M, and the energy unit of an A is ϵ as before. There are now also N B's with energy unit η. To make exchanges of energy possible we have to suppose, say, that there are present a few gas molecules, but that the latter never possess any sensible amount of energy. (Later on in § 12 we develop a method by which we shall be able to include any number of such molecules in our assembly.) We also require for the purposes of the proof to assume that ϵ and η are commensurable, but it does not matter how large the numbers may be which are required to express the ratio ϵ/η in its

lowest terms. To avoid introducing new symbols, we may suppose that the unit of energy is so chosen that ϵ and η are themselves integers without a common factor.

We have already introduced the idea of weight, and seen that we must assign the weight unity to every permissible state of a linear vibrator. To calculate the number of complexions of the assembly of any given sort, we have merely to calculate the number of ways in which the energy may be distributed among the vibrators, subject to the given statistical specification. A simple example will make the process clear.

Let there be two A's and two B's; let $\eta=2\epsilon$, $\mathrm{E}=4\epsilon$. Then the possible complexions are :—

$$\begin{matrix} \left\{\begin{matrix} aaaa \\ a'a'a'a' \end{matrix}\right. & \left\{\begin{matrix} aab \\ aab' \\ a'a'b \\ a'a'b' \end{matrix}\right. & \left\{\begin{matrix} bb \\ b'b' \end{matrix}\right. \\ \left\{\begin{matrix} aaaa' \\ aa'a'a' \end{matrix}\right. & \left\{\begin{matrix} aa'b \\ aa'b' \end{matrix}\right. & \\ aaa'a' & & bb' \end{matrix}$$

Here, for example, $aaaa'$ means that there is 3ϵ of energy on the first of the A's, ϵ on the second, and none on the B's. Each of the fourteen complexions is, by definition, of equal weight, and is therefore to be reckoned as of equal probability in the calculation of averages. Observe how with the small amount of energy available a good deal more goes into the smaller than into the larger quanta; for the pair of A's have on the average $\frac{16}{7}\epsilon$, as against $\frac{12}{7}\epsilon$ for the pair of B's.

We pass to the general case. The statistical state of the assembly is specified by sets of numbers a_r, b_s where a_r is the number of vibrators of type A which have energy $r\epsilon$, and b_s the number of B's with energy $s\eta$. All weights are unity and the number of complexions representing this statistical state is the number of indistinguishable ways (combinations) in which M vibrators can be divided into sets of $a_0, a_1 \ldots$ and at the same time N into sets $b_0, b_1 \ldots$. As illustrated by the example, it is therefore given by the formula

$$\frac{\mathrm{M}!}{a_0!\,a_1!\,a_2!\ldots}\,\frac{\mathrm{N}!}{b_0!\,b_1!\,b_2!\ldots} \quad . \quad . \quad . \quad . \quad (5{\cdot}1)$$

In (5·1) a_r and b_s may have any zero or positive values consistent with the conditions

$$\Sigma_r a_r=\mathrm{M}, \quad \Sigma_s b_s=\mathrm{N}, \quad \Sigma_r r\epsilon a_r+\Sigma_s s\eta b_s=\mathrm{E}, \quad . \quad (5{\cdot}2)$$

where E is the total energy of the system—necessarily an

integer in the units we employ. The total number C of all complexions is therefore

$$C=\Sigma_{a,b}\frac{M!}{a_0!\,a_1!\,a_2!\,\ldots}\frac{N!}{b_0!\,b_1!\,b_2!\,\ldots}, \quad . \quad . \quad (5{\cdot}3)$$

where the summation $\Sigma_{a,b}$ is to be carried out over all positive or zero values of a_r and b_s which satisfy (5·2).

By using (5·1) and (5·3) we can at once obtain an expression for the average value, taken over all complexions, of any quantity in which we are interested. We have already studied $\bar{a_r}$ in § 4. The main interest centres in $\bar{E}_A$, the average energy on the A's. We have at once

$$C\bar{E}_A=\Sigma_{a,b}\frac{(\Sigma_r r\epsilon a_r)M!\,N!}{a_0!\,a_1!\,a_2!\,\ldots\,b_0!\,b_1!\,b_2!\,\ldots} \quad . \quad . \quad . \quad (5{\cdot}4)$$

The following process leads to simple integrals to express the quantities C, $C\bar{E}_A$, etc. Consider the infinite series

$$(1+z^{\epsilon}+z^{2\epsilon}+\ldots\ldots)^M$$

expanded in powers of z by the multinominal theorem. The general term is

$$\frac{M!}{a_0!\,a_1!\,\ldots}z^{\Sigma_r r\epsilon a_r}.$$

It follows that if we select from the expansion of

$$(1+z^{\epsilon}+z^{2\epsilon}+\ldots)^M(1+z^{\eta}+z^{2\eta}+\ldots)^N. \quad . \quad (5{\cdot}5)$$

the coefficient of z^E, we shall obtain the sum of all possible terms such as (5·1) subject to the conditions (5·2), that is to say C. Similarly, if we form the expression

$$\left\{z\frac{d}{dz}(1+z^{\epsilon}+z^{2\epsilon}\ldots)^M\right\}(1+z^{\eta}+z^{2\eta}\ldots)^N, \quad . \quad (5{\cdot}6)$$

the general term in the first bracket must be

$$\frac{(\Sigma_r r\epsilon a_r)M!}{a_0!\,a_1!\,\ldots}z^{\Sigma_r r\epsilon a_r},$$

and by the same reasoning the coefficient of z^E in (5·6) must be $C\bar{E}_A$.

Expressions (5·5) and (5·6) are easily simplified— they are respectively

$$(1-z^{\epsilon})^{-M}(1-z^{\eta})^{-N}, \quad \left\{z\frac{d}{dz}(1-z^{\epsilon})^{-M}\right\}(1-z^{\eta})^{-N}.$$

The latter can also be written as

$$\left\{ -\mathrm{M}z\frac{d}{dz}\log(1-z^{\epsilon}) \right\}(1-z^{\epsilon})^{-\mathrm{M}}(1-z^{\eta})^{-\mathrm{N}}.$$

If these expressions are now expanded in powers of z by the binomial theorem, they give a sum of products of factorials which are, of course, the "homogeneous product" expressions used by Planck. It is possible to approximate to these by a legitimate use of Stirling's theorem and to replace the sums by integrals without much difficulty. It would, indeed, have been possible to start from these expressions, but we have not done so because in the general case to be discussed later that method would not be available. To make further progress by a method of general utility, we discard Stirling's theorem and express these coefficients of z^{E} by contour integrals taken round a circle γ with centre at the origin and radius less than unity. By well-known theorems on integration * we have at once

$$\mathrm{C}=\frac{1}{2\pi i}\int_{\gamma}\frac{dz}{z^{\mathrm{E}+1}}\frac{1}{(1-z^{\epsilon})^{\mathrm{M}}(1-z^{\eta})^{\mathrm{N}}}, \quad . \quad . \quad (5{\cdot}71)$$

$$\mathrm{C}\overline{\mathrm{E}}_{\mathrm{A}}=\frac{1}{2\pi i}\int_{\gamma}\frac{dz}{z^{\mathrm{E}+1}}\frac{-\mathrm{M}z\frac{d}{dz}\log(1-z^{\epsilon})}{(1-z^{\epsilon})^{\mathrm{M}}(1-z^{\eta})^{\mathrm{N}}} \quad . \quad . \quad (5{\cdot}72)$$

We can no longer hope for the single-term formulæ of §§ 3, 4. But (5·71) (5·72) are *exact*, and when M, N, E are all large in any definite fixed ratios, we can make use of the *method of steepest descents* to obtain simple adequate approximations. The method is very powerful and can be applied in a great number of cases without difficulty. Moreover, it is comparatively easy to use it with mathematical rigour if that is desired; and thus the somewhat clumsy calculations in the usual proofs of partition theorems are entirely avoided.

In general terms the process is this. Consider the integrand on the real positive axis. It becomes infinite at $z=0$ and again at $z=1$, and somewhere between at $z=\vartheta$ there is a minimum which is easily shown to be unique. Take as the contour the circle with centre at the origin and radius ϑ passing through this minimum. Then we find that, *for*

* For those not familiar with these theorems we may remark that $\frac{1}{2\pi i}\int_{\gamma} z^{r}dz=0$ when r is any integer other than -1, while $\frac{1}{2\pi i}\int_{\gamma}\frac{dz}{z}=1$: these equations at once give (5·71) and (5·72).

values of z on the contour, $z=\vartheta$ corresponds to a strong maximum, and when M, N, E are large, such a strong maximum that practically the whole value of the integral is contributed by the contour in the neighbourhood of this point. Hence in the integrals it is legitimate to substitute the value at this point for any factors which do not themselves show strong maxima here or elsewhere. On this general principle we can remove the term $-\mathrm{M}z\dfrac{d}{dz}\log(1-z^{\epsilon})$ from under the integral sign, provided that z is given the value ϑ determined by the maximum condition. The part of the integrand involving the large numbers M, N, E, determines the value of ϑ as being the unique real positive fractional root of the equation

$$\frac{d}{dz}\left\{z^{-\mathrm{E}}(1-z^{\epsilon})^{-\mathrm{M}}(1-z^{\eta})^{-\mathrm{N}}\right\}=0.$$

That is, ϑ satisfies the equation :

$$\mathrm{E}=\frac{\mathrm{M}\epsilon}{\vartheta^{-\epsilon}-1}+\frac{\mathrm{N}\eta}{\vartheta^{-\eta}-1}. \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}8)$$

The remaining integrands in C and CE_{A} are identical, and we therefore have

$$\overline{\mathrm{E}_{\mathrm{A}}}=-\mathrm{M}\vartheta\frac{d}{d\vartheta}\log(1-\vartheta^{\epsilon}),$$

$$=\frac{\mathrm{M}\epsilon}{\vartheta^{-\epsilon}-1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}9)$$

If a similar process is carried out for the B's, we have

$$\overline{\mathrm{E}_{\mathrm{B}}}=\frac{\mathrm{N}\eta}{\vartheta^{-\eta}-1}, \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}91)$$

in agreement with the necessary relation

$$\overline{\mathrm{E}_{\mathrm{A}}}+\overline{\mathrm{E}_{\mathrm{B}}}=\mathrm{E}.$$

Equations (5·9) (5·91) determine the partition of energy and take their familiar form if we replace ϑ by $e^{-1/kT}$. We shall return to this point later.

§ 6. *Application of the Method of Steepest Descents.*

After this sketch it will be well to establish the validity of the ar uments used. This section is put in for mathematical completeness, and is not concerned at all with physical questions. We treat of a more general case than that of § 5.

Arguments of this type—asymptotic expansions by steepest descents—are, of course, well known in pure mathematics.

Consider a contour integral of the form

$$\frac{1}{2\pi i}\int_\gamma \mathrm{F}(z)[\phi(z)]^{\mathrm{E}}\frac{dz}{z}, \quad . \quad . \quad . \quad . \quad (6{\cdot}1)$$

subject to the following conditions:—

(i.) $\phi(z)$ is an analytic function of z, which can be expanded in a series of ascending powers of z.
(ii.) This series starts with some negative power.
(iii.) Every coefficient is real and positive.
(iv.) Its circle of convergence is of radius unity. (This condition is quite unessential to the mathematics, but makes the statement simpler, and is physically true.)
(v.) The powers that occur in the series cannot all be put in the form $\alpha+\beta r$ where α and β are any given integers and r takes all integer values.
(vi.) $\mathrm{F}(z)$ is an analytic function with no poles in the unit circle, except perhaps at the origin.
(vii.) γ is a closed contour going once counterclockwise round the origin.

The problem is to obtain the asymptotic value as E tends through integer values to infinity.

We shall first study the properties of $\phi(z)$. Considering real values, it must have one and only one minimum between 0 and 1. For it is continuous and tends to $+\infty$ at both 0 and 1, and so must have at least one minimum between. Further, to find minima we differentiate, and then all the negative powers will have negative coefficients and all the positive positive. It follows that minima are given where two curves cut, one of which decreases steadily between 0 and 1, while the other increases steadily. These curves can only cut in one point, and so there is only one minimum. Next, for the complex values, consider a circle of any radius r less than 1. As the modulus of a sum is never greater than the sum of the moduli, it follows that at no point on this circle can $|\phi(z)|$ be greater than $\phi(r)$. Moreover, it can only equal $\phi(r)$ provided that condition (v.) is broken, and in that case there will be β points at each of which $|\phi(z)|=\phi(r)$. We can thus see that on account of the large exponent it is only the part of γ near the real axis that contributes effectively to the asymptotic value of the integral. This suggests

the substitution $z=re^{i\alpha}$, with α as the new variable of integration. Expanding near the real axis we have

$$[\phi(z)]^{\mathrm{E}}=[\phi(r)]^{\mathrm{E}}\exp.\{i\alpha\mathrm{E}r\phi'/\phi+O(\mathrm{E}\alpha^2)\}. \quad (6{\cdot}11)$$

This function contains a periodic term of high frequency which cuts down the contributions for small values of α, so that the value of the integral will in general depend on more distant parts of the contour than those to which this approximation will apply. But if we choose for r the special value ϑ corresponding to the unique minimum $\phi'=0$, then the oscillating term in the exponential vanishes and the contributions for small values of α dominate the whole integral. For this special value of r the exponential becomes

$$\exp.\{-\tfrac{1}{2}\mathrm{E}\alpha^2\vartheta^2\phi''/\phi+O(\mathrm{E}\alpha^3)\}, \quad . \quad . \quad (6{\cdot}12)$$

and by (iii.) $\phi''>0$. We see at once that we can suppose that $\mathrm{E}^{\frac{1}{2}}\alpha$ ranges effectively over all values from $-\infty$ to $+\infty$ while all other terms, such as $\alpha, \ldots, \mathrm{E}\alpha^3, \ldots$ remain small. We then obtain for (6·1) on putting $z=\vartheta e^{i\alpha}$ the asymptotic expression

$$\frac{1}{2\pi}[\phi(\vartheta)]^{\mathrm{E}}\int_{-\infty}^{+\infty}\{\mathrm{F}(\vartheta)+i\alpha\vartheta\mathrm{F}'(\vartheta)+O(\alpha^2)+O(\mathrm{E}\alpha^3)\}e^{-\frac{1}{2}\mathrm{E}\alpha^2\vartheta^2\phi''}\phi\,d\alpha.$$

For most purposes the first term in the expansion will suffice, but if the precise values of the fluctuations are required, the second also is necessary. As it is in general rather complicated, we shall content ourselves here with pointing out its order of magnitude.

On carrying through the necessary calculations we find

$$\frac{\phi^{\mathrm{E}}}{(2\pi\mathrm{E}\vartheta^2\phi''/\phi)^{\frac{1}{2}}}\left[\mathrm{F}-\frac{\{\vartheta,\phi,\mathrm{F}\}}{2\mathrm{E}\vartheta^2\phi'/\phi}\right]. \quad . \quad . \quad (6{\cdot}2)$$

The argument of F and ϕ is everywhere ϑ; the term $\{\vartheta,\phi,\mathrm{F}\}$ denotes a complicated expression of ϑ,ϕ and its first four derivatives, and F and its first two derivatives, but is independent of E. If condition (v.) is dropped, we shall have β equal maxima arranged round the circle γ, and, provided F has the same value at each of them, the integral will have a value equal to (6·2) multiplied by β.

Now consider the problem of § 5, to which our work applies immediately with

$$\phi=z^{-1}(1-z^{\epsilon})^{-\mathrm{M}/\mathrm{E}}(1-z^{\eta})^{-\mathrm{N}/\mathrm{E}}. \quad . \quad . \quad . \quad (6{\cdot}3)$$

We may suppose that E tends to infinity and also M and N

in such a way that M/E and N/E are constant. This function satisfies all the conditions of this section—the fact that it is in general many-valued is irrelevant, for we are only concerned with that particular branch which is real when z is real and $0<z<1$ and this branch is one-valued in the unit circle. The unique minimum ϑ is determined by the equation $\phi'=0$ or

$$\mathrm{E}=\frac{\mathrm{M}\epsilon}{\vartheta^{-\epsilon}-1}+\frac{\mathrm{N}\eta}{\vartheta^{-\eta}-1}. \quad . \quad . \quad . \quad . \quad . \quad (6{\cdot}4)$$

The value of the integral (5·71) is then by (6·2) (omitting the second term the form of which is only required in calculating fluctuations),

$$\mathrm{C}=\frac{\vartheta^{-\mathrm{E}}(1-\vartheta^{\epsilon})^{-\mathrm{M}}(1-\vartheta^{\eta})^{-\mathrm{N}}}{\{2\pi\mathrm{E}\vartheta^{2}\phi''/\phi\}^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad (6{\cdot}5)$$

If, contrary to hypothesis, we had taken ϵ and η as having a common factor β, condition (v.) would have been violated. In this case C would be β times as great as before, but so would $\mathrm{C}\bar{\mathrm{E}}_{\mathrm{A}}$, so that $\bar{\mathrm{E}}_{\mathrm{A}}$ and all other averages would be unaffected. The use of (6·2) to evaluate $\mathrm{C}\bar{\mathrm{E}}_{\mathrm{A}}$ (5·72) etc. leads at once to expressions similar to (6·5), and so to the results given formally in the last section and to others to be given later.

As we shall see, ϑ is the temperature measured on a special scale, and there is great advantage in regarding ϑ, rather than E, as the independent variable which determines the state of the assembly. If this is done the expression $\mathrm{E}\vartheta^{2}\phi''/\phi$ can be put into simpler form. For it is easily verified that

$$\mathrm{E}\vartheta^{2}\phi''/\phi=\frac{\mathrm{M}\epsilon^{2}\vartheta^{-\epsilon}}{(\vartheta^{-\epsilon}-1)^{2}}+\frac{\mathrm{N}\eta^{2}\vartheta^{-\eta}}{(\vartheta^{-\eta}-1)^{2}},$$

$$=\vartheta\frac{d}{d\vartheta}(\bar{\mathrm{E}}_{\mathrm{A}}+\bar{\mathrm{E}}_{\mathrm{B}})=\vartheta\frac{d\mathrm{E}}{d\vartheta}, \quad . \quad . \quad (6{\cdot}6)$$

if E is regarded as a function of ϑ, given by (5·8).

It may be remarked that the constant occurrence of the operator $\vartheta d/d\vartheta$ suggests a change of variable to $\log\vartheta$. Though this has some advantages we have not adopted it, partly because it makes the initial argument about the multinomial theorem a little harder to follow and complicates the contour of the integration, and also because $\log\vartheta$ is not itself the absolute temperature—if it had been, the physical simplicity might have outweighed the other objections—but only a quantity proportional to its reciprocal.

§ 7. *The Meaning of* ϑ.

Returning to the subject of § 5, we see that the partition of energy between the A's and the B's depends on a parameter which can be determined in terms of the energy by means of the equation (5·8). It is fairly evident that ϑ is connected with the temperature, though it requires more general considerations to prove this properly. But if we assume this connexion and are content to replace the thermodynamic definition of absolute temperature by one based on the law of equipartition of energy for systems obeying the laws of classical mechanics, then we can at once identify the meaning of ϑ.

For let us suppose that the B's are vibrators of very low frequency. They will then obey the classical laws, and the average energy of each will be $k\mathrm{T}$. But

$$\mathrm{Lt}_{\eta\to 0}\frac{\eta}{\vartheta^{-\eta}-1}=\frac{1}{\log(1/\vartheta)}=k\mathrm{T},$$

which shows that

$$\vartheta=e^{-1/k\mathrm{T}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7\cdot1)$$

Substituting this in (5·9), we obtain the well-known form

$$\overline{\mathrm{E}}_{\mathrm{A}}=\frac{\mathrm{M}\epsilon}{e^{\epsilon/k\mathrm{T}}-1}.$$

Observe that while η is tending to zero there need be no difficulty about the condition that η and ϵ are to be commensurable. We shall later return to this question of temperature and establish it for much more general types of system.

§ 8. *Other mean values.*

Exactly the same methods can be applied to evaluate any other mean value besides E_{A}. For example :—

$$\overline{Ca}_r=\Sigma_{a,b}\,a_r\,\frac{\mathrm{M}!}{a_0!\,a_1!\ldots.}\,\frac{\mathrm{N}!}{b_0!\,b_1!\ldots.},$$

$$=\mathrm{M}\Sigma_{a',b}\frac{(\mathrm{M}-1)!}{a_0'!\,a_1'!\ldots.}\,\frac{\mathrm{N}!}{b_0!\,b_1!\ldots.}, \quad . \quad (8\cdot1)$$

summed over all zero and positive values such that

$$\Sigma_r a_r'=\mathrm{M}-1,\ \Sigma_s b_s=\mathrm{N},\ \Sigma_r r\epsilon a_r'+\Sigma_s s\eta b_s=\mathrm{E}-r\epsilon.$$

Applying the multinomial theorem and reducing the

expression to a complex integral, we have

$$C\overline{a}_r = M\frac{1}{2\pi i}\int_\gamma z^{-E+1}\frac{z^{r\epsilon}}{(1-z^\epsilon)^{M-1}(1-z^\eta)^N}, \quad . \quad (8{\cdot}2)$$

which, by virtue of the value of C from (5·71) and the argument of § 6, at once yields

$$\begin{aligned}\overline{a}_r &= M\vartheta^{r\epsilon}(1-\vartheta^\epsilon),\\ &= Me^{-r\epsilon/kT}(1-e^{-\epsilon/kT}), \quad . \quad . \quad . \quad . \quad (8{\cdot}3)\end{aligned}$$

which is the formula of § 4 over again, the presence of the B's being immaterial.

When we come to evaluate fluctuations the matter is a little more complicated, because the leading terms cut out, and so the second term of the asymptotic expansion will in general play a part. For example, consider the fluctuations of a_r:

$$\overline{(a_r-\overline{a}_r)^2} = \overline{a_r(a_r-1)} + \overline{a}_r - (\overline{a}_r)^2.$$

By arguments exactly similar to those above, we have

$$C\overline{a_r(a_r-1)} = M(M-1)\frac{1}{2\pi i}\int_\gamma z^{-E+1}\frac{z^{2r\epsilon}}{(1-z^\epsilon)^{M-2}(1-z^\eta)^N},$$

and so by (6·2)

$$\overline{a_r(a_r-1)} = M(M-1)\vartheta^{2r\epsilon}(1-\vartheta^\epsilon)^2\{1+O(1/E)\}.$$

Thus the fluctuation is

$$\overline{a}_r - M\vartheta^{2r\epsilon}(1-\vartheta^\epsilon)^2 + O(M^2/E).$$

This is sufficient to show that the possession of $\overline{a}_r$ (8·3) is a normal property of the assembly.

The complete calculation of the O-term is rather complicated; the result is given at the end of this section. But a great simplification arises if we suppose that there are many more B's than A's, while E is so adjusted that ϑ the temperature is unchanged. In this case the term $O(M^2/E)$ becomes small and may be neglected. We shall describe this case by saying that A is in a bath of temperature ϑ. Then, provided this is so, we have

$$\overline{(a_r-\overline{a}_r)^2} = \overline{a}_r(1-\overline{a}_r/M). \quad . \quad . \quad . \quad . \quad (8{\cdot}4)$$

A much more important quantity is the fluctuation of E_A. This is found by evaluating $\overline{E_A^2}$. Now, just as $C\overline{E}_A$ was given by operating with zd/dz on the first factor in

$(1-z^\epsilon)^{-M}(1-z^\eta)^{-N}$, so $C\overline{E_A^2}$ is easily seen to be given by operating with $\left(z\frac{d}{dz}\right)^2$ in the same way. Thus

$$C\overline{E_A^2}=\frac{1}{2\pi i}\int_\gamma \frac{dz}{z^{E+1}}\left\{\left(z\frac{d}{dz}\right)^2(1-z^\epsilon)^{-M}\right\}(1-z^\eta)^{-N}.$$

If we again suppose an infinite bath of temperature ϑ, we can omit the second term of the asymptotic expansion (6·2) and obtain

$$\begin{aligned}\overline{E_A^2}&=(1-\vartheta^\epsilon)^M\left\{\left(\vartheta\frac{d}{d\vartheta}\right)^2(1-\vartheta^\epsilon)^{-M}\right\},\\&=(1-\vartheta^\epsilon)^M\vartheta\frac{d}{d\vartheta}\left\{\overline{E_A}(1-\vartheta^\epsilon)^{-M}\right\},\\&=(\overline{E_A})^2+\vartheta\frac{d\overline{E}_A}{d\vartheta},\end{aligned}$$

and so the fluctuation is

$$\left.\begin{aligned}(E_A-\overline{E_A})^2&=E_A^2-(\overline{E_A})^2,\\&=\vartheta\frac{d\overline{E}_A}{d\vartheta},\\&=kT^2\frac{d\overline{E}_A}{dT}.\end{aligned}\right\}\quad\ldots\quad(8\cdot5)$$

This is a result of which Einstein * made use in his work on fluctuations of radiation. It should be emphasized that these results are only accurate in a temperature bath, and not when the number of systems A is a finite fraction of the assembly.

In all cases (6·2) shows that the possession of $\overline{E}_A$ is a normal property of the assembly.

If we work out exactly the second terms in the asymptotic formulæ of § 6 and apply them to the fluctuations of a_r and E_A we find

$$\overline{(a_r-\overline{a_r})^2}=\overline{a_r}\left[1-\frac{\overline{a_r}}{M}\left\{1+\frac{M(r\epsilon-\overline{E}_A/M)^2}{\vartheta\,dE/d\vartheta}\right\}\right],\quad(8\cdot6)$$

$$\overline{(E_A-\overline{E}_A)^2}=\vartheta\frac{d\overline{E}_A}{d\vartheta}\left(1-\vartheta\frac{d\overline{E}_A}{d\vartheta}\Big/\vartheta\frac{dE}{d\vartheta}\right).\quad\ldots\quad(8\cdot7)$$

Formula (4·6) above is a special case of (8·6).

* A. Einstein, *Phys. Zeitschr.* vol. x. p. 185 (1909).

Finally it is of some interest to point out that we can obtain a formula for $\overline{(E_A - E_A)^{2s}}$ of general validity. We have in fact

$$\overline{(E_A - E_A)^{2s}} = 1.3 \ldots (2s-1)\{\overline{(E_A - E_A)^2}\}^s, \quad . \quad (8{\cdot}8)$$

where $\overline{(E_A - E_A)^2}$ is given by (8·7). We retain of course only the highest order term *, which is thus $O(\overline{E_A})^s$.

§ 9. *Generalization to any number of types of system, and to systems of any quantized character.*

It is clear that the present method of treating partitions is of a much more general character than has so far been exhibited. Consider an assembly composed of two types, A and B, of quantized systems more complicated than Planck vibrators. We suppose generally that the systems of type A, M in number, can take energies to the extents $\epsilon_0, \epsilon_1, \epsilon_2, \ldots$, and these states have *weight* factors $p_0, p_1, p_2, \ldots$ in conformity with the discussion in § 2. Similarly, the B's, N in number, can take energies $\eta_0, \eta_1, \eta_2, \ldots$ with weights $q_0, q_1, q_2, \ldots$. We have to suppose that it is possible to determine a basal unit of energy such that all the ϵ's and η's can be expressed as integers. Further, it simplifies the work if we suppose that there is no factor common to all of them. Proceeding exactly as before, we set down the weighted number of complexions which correspond to the specification that, of the A's, a_r have energy ϵ_r; of the B's, b_s have energy η_s. This number is

$$\frac{M!}{a_0!\, a_1! \ldots} p_0^{a_0} p_1^{a_1} \ldots \cdot \frac{N!}{b_0!\, b_1! \ldots} q_0^{b_0} q_1^{b_1} \ldots, \quad . \quad (9{\cdot}1)$$

and the a's and b's are able to take all values consistent with

$$\Sigma_r a_r = M, \quad \Sigma_s b_s = N, \quad \Sigma_r \epsilon_r a_r + \Sigma_s \eta_s b_s = E. \quad . \quad (9{\cdot}2)$$

Now form the functions

$$f(z) = p_0 z^{\epsilon_0} + p_1 z^{\epsilon_1} + p_2 z^{\epsilon_2} + \ldots, \quad . \quad . \quad . \quad (9{\cdot}3)$$

$$g(z) = q_0 z^{\eta_0} + q_1 z^{\eta_1} + q_2 z^{\eta_2} + \ldots \quad . \quad . \quad . \quad (9{\cdot}31)$$

These will be called the *partition functions* † of the types of

* *Cf.* Gibbs' 'Statistical Mechanics,' p. 78. But (8·8) is generally valid, while Gibbs' formulæ really refer only to a group of systems in a temperature bath.

† They are practically the "Zustandsumme" of Planck, 'Radiation Theory,' p. 127.

system A and B. The application of the multinomial theorem then leads to the consideration of the expression

$$[f(z)]^{\mathrm{M}}[g(z)]^{\mathrm{N}},$$

and pursuing exactly the same course as in § 5, we find

$$\mathrm{C}=\frac{1}{2\pi i}\int_{\gamma}\frac{dz}{z^{\mathrm{E}+1}}[f(z)]^{\mathrm{M}}[g(z)]^{\mathrm{N}}, \quad . \quad . \quad . \quad (9{\cdot}4)$$

$$\mathrm{C}\overline{\mathrm{E}}_{\mathrm{A}}=\frac{1}{2\pi i}\int_{\gamma}\frac{dz}{z^{\mathrm{E}+1}}\left\{z\frac{d}{dz}[f(z)]^{\mathrm{M}}\right\}[g(z)]^{\mathrm{N}}. \quad (9{\cdot}5)$$

Assume for the moment that we can choose a $\phi(z)$ conforming to the requirements of § 6. The whole calculation then goes on as before. The radius of the circle to be taken as contour is given by the equation

$$\mathrm{E}=\mathrm{M}\vartheta\frac{d}{d\vartheta}\log f(\vartheta)+\mathrm{N}\vartheta\frac{d}{d\vartheta}\log g(\vartheta). \quad . \quad . \quad (9{\cdot}6)$$

This equation has one and only one root. We thus can at once put down

$$\left.\begin{aligned}\overline{\mathrm{E}}_{\mathrm{A}}&=[f(\vartheta)]^{-\mathrm{M}}\vartheta\frac{d}{d\vartheta}[f(\vartheta)]^{\mathrm{M}},\\&=\mathrm{M}\vartheta\frac{d}{d\vartheta}\log f(\vartheta).\end{aligned}\right\} \quad . \quad . \quad . \quad (9{\cdot}7)$$

In exactly the same way we have

$$\overline{a}_r=\mathrm{M}p_r\vartheta^{\epsilon_r}/f(\vartheta), \quad . \quad . \quad . \quad . \quad . \quad (9{\cdot}8)$$

and we can also verify that in the case of an infinite bath the fluctuations are again given by (8·4), (8·5), and that equation (6·6) is still true. The exact forms of the fluctuations (8·6), (8·7) are also valid if we replace $r\epsilon$ by ϵ_r.

We have now to examine whether $\phi(z)$ can be properly chosen. It is natural to take

$$\phi(z)=z^{-1}[f(z)]^{\mathrm{M}\,\mathrm{E}}[g(z)]^{\mathrm{N}\,\mathrm{E}}. \quad . \quad . \quad . \quad (9{\cdot}81)$$

By its definition it must satisfy (i.). For (ii.) to be true, we must have

$$\mathrm{E}>\mathrm{M}\epsilon_0+\mathrm{N}\eta_0,$$

which is the trivial condition that there must be enough energy to provide each system with the least amount of energy it is permitted to have. Condition (iv.) does not appear at first sight inevitable, but must follow from Bohr's Correspondence Principle *, for the convergence of the series $f(z)$ and $g(z)$ depends on their later terms—that is, those of

* Bohr, *loc. cit.*

large quantum numbers. Condition (v.) is satisfied if not all the ϵ's and η's have a common factor. There remains (iii.), and here there are trivial analytical difficulties when, as in general, M/E and N/E are fractional.

It is, however, easy to generalize § 6 by replacing $[\phi(z)]^E$ by

$$z^{-E}[f(z)]^M[g(z)]^N,$$

and letting E, M, N all tend to infinity independently. Condition (iii.) is then satisfied, as can be seen by multiplying out, and so all the conditions are satisfied, and the final results stated above are unaffected.

Finally, we may observe that all our results can be extended at once to an assembly containing any number of types of system. If there are M_c systems of type C, for which the partition function is $f_c(\vartheta)$, then

$$\bar{E}_c = M_c \vartheta \frac{d}{d\vartheta} \log f_c(\vartheta),$$

where ϑ is determined by

$$E = \Sigma_c M_c \vartheta \frac{d}{d\vartheta} \log f_c(\vartheta).$$

The formal validity of the proof will require all the quantities ϵ_r to be commensurable. It will be shown in § 12 how this restriction may be removed.

§ 10. *Vibrators of two and three degrees of freedom.*

As a first example we take a set of vibrators each of which is free to vibrate in a plane under a central force proportional to the distance. The sequence of energies is again 0, ϵ, 2ϵ, ..., but the weights are no longer unity, as the system is degenerate. Following the principle laid down in § 2, we may evaluate the weights by treating the system as non-degenerate and counting the number of different motions which have the same total quantum number. Now we can quantize the plane vibrators in directions x and y, and as an example for the case 2ϵ, we have three alternatives $(2\epsilon, 0)$, (ϵ, ϵ), $(0, 2\epsilon)$. This is easily generalized, and gives to $r\epsilon$ the weight $r+1$. The partition function for these vibrators is thus

$$f(z) = 1 + 2z + 3z^2 + 4z^3 + \ldots,$$
$$= (1-z)^{-2}.$$

From the general theorem (9·7) we at once have

$$\overline{E}_A = \frac{2M\epsilon}{\vartheta^{-\epsilon}-1},$$

so that such vibrators have just twice as much energy as the line vibrators.

In exactly the same way we can treat the case of three dimensions. To illustrate the weights we again take the case of 2ϵ and quantize the system in x, y, z. There are six alternatives $(2\epsilon, 0, 0)$, $(0, 2\epsilon, 0)$, $(0, 0, 2\epsilon)$, $(\epsilon, \epsilon, 0)$, $(\epsilon, 0, \epsilon)$, $(0, \epsilon, \epsilon)$. The general form for $r\epsilon$ is $\frac{1}{2}(r+1)(r+2)$. The partition function is now

$$f(z) = 1 + 3z + 6z^2 + 10z^3 + \ldots,$$
$$= (1-z)^{-3},$$

which leads at once to the expected result

$$\overline{E}_A = \frac{3M\epsilon}{\vartheta^{-\epsilon}-1}.$$

§ 11. *Rotating Molecules.*

Another interesting example to which the calculations at once apply is that part of the specific heat of a gas due to the rotations of the molecules. Various writers * have quantized the motions of a rigid body, and it is found that the system has at most two instead of three periods, so that it is partly degenerate. We may consider for simplicity a diatomic molecule. Then, on account of the small moment of inertia about the line of centres, the third degree of freedom may be omitted altogether—its quantum of energy is too large. A simple calculation then leads to energies of rotation ϵ_r given by

$$\epsilon_r = \frac{h^2}{8\pi^2 I} r^2, \quad \ldots\ldots \quad (11\cdot1)$$

where I is the moment of inertia about a transverse axis, which we shall assume to be independent of r. This is a degenerate system, and considerations of the number of cases which occur if it is quantized for the two degrees shows that the weight to be attached is $2r+1$. This is on the principles suggested by Bohr † with a simplifying modification; for Bohr had to suppose that certain quantized motions were excluded for other reasons which are not operative

* Among others, Ehrenfest, *Verh. Deutsch. Phys. Ges.* xv. p. 451 (1913). Epstein, *Phys. Zeitschr.* xx. p. 289 (1919). F. Reiche, *Ann. der Physik*, liv. p. 421 (1917).

† *Loc. cit.* p. 26.

here *. There can, we think, be no question as to the correctness of the weight $2r+1$, but most recent writers have used a factor r: our formula for the specific heat has therefore a rather different value.

We may now apply our general formulæ to this case with

$$p_r=2r+1,\ \epsilon_r=r^2\epsilon,\ \epsilon=\frac{h^2}{8\pi^2 I}. \quad . \quad . \quad (11{\cdot}2)$$

Then
$$f(\vartheta)=1+3\vartheta^{\epsilon}+5\vartheta^{4\epsilon}+7\vartheta^{9\epsilon}+\ldots, \quad . \quad . \quad (11{\cdot}3)$$

$$\mathrm{E_A}=\mathrm{M}\vartheta\frac{d}{d\vartheta}\log f(\vartheta). \quad . \quad . \quad . \quad . \quad . \quad (11{\cdot}31)$$

The contribution of the rotations to the molecular specific heat, C_{rot}, is $d\overline{\mathrm{E}}_{\mathrm{A}}/d\mathrm{T}$, where M must be taken as the number of molecules in one gramme-molecule of gas. Thus, using (7·1), we have

$$\mathrm{C}_{rot}=\frac{\mathrm{M}k}{(\log\vartheta)^2}\left(\vartheta\frac{d}{d\vartheta}\right)^2\log f(\vartheta), \quad . \quad . \quad (11{\cdot}4)$$

and $\mathrm{M}k=\mathrm{R}$, the usual gas constant. If we write

$$\sigma=\frac{h^2}{8\pi^2 Ik\mathrm{T}}, \quad . \quad . \quad . \quad . \quad . \quad (11{\cdot}5)$$

then

$$\mathrm{C}_{rot}=\mathrm{R}\sigma^2\frac{d^2}{d\sigma^2}\log\left(1+3e^{-\sigma}+5e^{-4\sigma}+7e^{-9\sigma}+\ldots\right). \quad (11{\cdot}51)$$

Equation (11·5) shows that, when $\mathrm{T}\to\infty$, $\sigma\to 0$. It can be shown by the application of standard theorems on series † that when $\sigma\to 0$,

$$\mathrm{C}_{rot}\to\mathrm{R}, \quad . \quad . \quad . \quad . \quad . \quad (11{\cdot}52)$$

which is the correct limiting value as required by classical dynamics.

In the general case of any body we have three degrees of rotational freedom, the motion is simply degenerate ‡, and the energy enters as a sum of square numbers multiplying two units of energy. The motion of the axis of symmetry and the motion about the axis of symmetry are not independent, and it is impossible therefore for the partition function to split up into the product of two partition functions which represent the separate contributions of the two motions. The result is a *double* series of the same general type as (11·3).

* Assuming that no extraneous considerations rule out any of these states.

† Bromwich, Infinite Series, p. 132. The theorem is due to Cesàro.

‡ Epstein, *Phys. Zeit* xx. p. 289 (1919).

It does not appear profitable to examine these expressions further here, since the agreement with experiment is not very good at all temperatures. It is to be presumed that the assumption of constant moments of inertia is at fault, and this is supported by some of the evidence from band spectra; further, it is probable that the case of no rotation must be excluded, involving the omission of the first term in the partition functions. The discussion of the practical applications of these formulæ cannot be entered into here.

§ 12. *Assemblies containing free molecules.*

The problems we have so far discussed have all possessed the distinguishing characteristic that the temperature is the only independent variable. As soon as we treat of free molecules this is no longer the case, for now the volume must be another independent variable. Nevertheless, as we shall see, the same methods of calculation are available. The partition is no longer represented exactly by integrals, as it was for the quantized motions, but from the nature of the case some form of limiting process is required. The free molecules cannot of course be regarded as the limit of three-dimensional vibrators of low frequency, for they have no potential energy to share in the partition. We must proceed by the method common to most discussions of the distribution laws of classical assemblies—divide up into cells the six-dimensional space in which the state of any molecule is represented, associate with each cell a certain constant value of the energy, and in the limit make all the dimensions of all the cells tend to zero *.

We take an assembly composed of M systems of the type A of § 9 and P free-moving monatomic molecules of mass m and of small size, the whole enclosed in a vessel of volume V. The energy of the molecules is solely their energy of translation; they are supposed to obey the laws of classical mechanics (except during their collisions with the A's). In order to specify the state of the assembly, we take a six-dimensional space of co-ordinates q_1, q_2, ... p_3, the three rectangular co-ordinates and momenta of a molecule in the vessel. We divide up this space into small cells, 1, 2, 3, ..., t ..., of extensions $(dq_1 \ldots dp_3)_t$, which may or may not be

* That the limit of the distribution laws worked out for the cells is the true distribution law for the actual assembly is an *assumption* implicit in all such discussions.

equal. Then by the principles of § 2 the weight factor for the tth cell is

$$\delta_t = \frac{(dq_1 \ldots dp_3)_t}{h^3}, \quad . \quad . \quad . \quad . \quad . \quad (12{\cdot}1)$$

provided of course that the cell is relevant to our assembly. Only those cells have a weight for which the q's lie in the vessel; but the p's may range over all values from $-\infty$ to $+\infty$, for the method of summation will automatically exclude values which could not be allowed. Associated with the tth cell there is energy given by

$$\zeta_t = \frac{1}{2m}(p_1^2 + p_2^2 + p_3^2). \quad . \quad . \quad . \quad (12{\cdot}11)$$

The state of the molecules in the assembly is specified by the numbers $c_1, c_2, \ldots$ of molecules in cells 1, 2, ... The specification of the A's is as before. The number of weighted complexions corresponding to the specification is then

$$\frac{\mathrm{M}!}{a_0!\, a_1! \ldots} p_0^{a_0} p_1^{a_1} \ldots \frac{\mathrm{P}!}{c_1!\, c_2! \ldots} \delta_1^{c_1} \delta_2^{c_2} \ldots, \quad . \quad (12{\cdot}12)$$

where $$\Sigma_r a_r = \mathrm{M}, \ \Sigma_t c_t = \mathrm{P}, \ \Sigma_r a_r \epsilon_r + \Sigma_t c_t \zeta_t = \mathrm{E}. \quad . \quad (12{\cdot}13)$$

In proceeding thus we are constructing an artificial assembly in which the energy is taken to have the same value ζ_t in all parts of the tth cell, and in which all the ζ's and all the ϵ's can be expressed as multiples of some basal unit, without a factor common to them all.

This assembly can be made to resemble the real one to any standard of approximation required. For such an artificial assembly we can make use of the whole of our machinery. The results all depend on integrals such as

$$\mathrm{C} = \frac{1}{2\pi i} \int_\gamma \frac{dz}{z^{\mathrm{E}+1}} [f(z)]^{\mathrm{M}} [h(z)]^{\mathrm{P}}, \quad . \quad . \quad (12{\cdot}2)$$

where the partition function of the artificial molecules is

$$h(z) = \Sigma_t \delta_t z^{\zeta_t}, \quad . \quad . \quad . \quad . \quad . \quad (12{\cdot}21)$$

and the formulæ of § 8 follow at once for $\overline{\mathrm{E}_C}$, $\overline{(\mathrm{E}_C - \mathrm{E}_C)^2}$, $\overline{c_t}$ and $\overline{(c_t - c_t)^2}$. These results give completely the exact partition laws for any artificial assembly of the type considered. To obtain the actual distribution law for the real assembly, we must make all the dimensions of all the cells tend to zero, and obtain the limit of the partition function. Now, by the

definition of an integral, in the limit $h(\vartheta)\to\mathrm{H}(\vartheta)$, where

$$\mathrm{H}(\vartheta)=\frac{1}{h^3}\int^{(6)} e^{-\frac{\log 1/\theta}{2m}(p_1^2+p_2^2+p_3^2)}\,dq_1\ldots dp_3\,. \quad (12{\cdot}3)$$

The integration is over the volume V and over all values of the p's from $-\infty$ to $+\infty$. This gives at once

$$\mathrm{H}(\vartheta)=\frac{(2\pi m)^{3/2}\mathrm{V}}{h^3(\log 1/\vartheta)^{3/2}}. \quad . \quad . \quad . \quad . \quad (12{\cdot}4)$$

In the formulæ the functions $dh/d\vartheta$ and $d^2h/d\vartheta^2$ also occur, and it is easily shown directly that their limits are $d\mathrm{H}/d\vartheta$ and $d^2\mathrm{H}/d\vartheta^2$. We may therefore use (12·4) throughout for the real assembly, and at once obtain the following expressions:

$$\bar{\mathrm{E}}_c=\frac{\frac{3}{2}\mathrm{P}}{\log 1/\vartheta}=\tfrac{3}{2}\mathrm{P}k\mathrm{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12{\cdot}5)$$

$$c_t=\frac{\mathrm{P}}{\mathrm{V}}\left(\frac{m\log 1/\vartheta}{2\pi}\right)^{3/2} e^{-\frac{1}{2}(\log 1/\theta)m(u^2+v^2+w^2)}\,dx\,dy\,dz\,du\,dv\,dw, \quad . \quad . \quad . \quad . \quad (12{\cdot}51)$$

$$=\frac{\mathrm{P}}{\mathrm{V}}\left(\frac{m}{2\pi k\mathrm{T}}\right)^{3/2} e^{-\frac{m}{2k\mathrm{T}}(u^2+v^2+w^2)}\,dx\ldots dw. \quad . \quad . \quad . \quad (12{\cdot}52)$$

The temperature ϑ is determined by

$$\mathrm{E}=\mathrm{M}\vartheta\frac{d}{d\vartheta}\log f(\vartheta)+\tfrac{3}{2}\mathrm{P}\frac{1}{\log(1/\vartheta)}, \quad . \quad (12{\cdot}53)$$

and the fluctuation of energy of the molecules in a bath of temperature ϑ is given by

$$(\mathrm{E}_c-\bar{\mathrm{E}}_c)^2=\vartheta\frac{d}{d\vartheta}\mathrm{E}_c=\tfrac{3}{2}\mathrm{P}k^2\mathrm{T}^2 \quad . \quad . \quad (12{\cdot}54)$$

If the fluctuation of c_t is evaluated, it takes the simple value

$$(c_t-\bar{c}_t)^2=\bar{c}_t, \quad . \quad . \quad . \quad . \quad . \quad (12{\cdot}55)$$

whether it is in a bath or not; for the second factor, analogous to that in (8·4), can be omitted when the cell is taken to be of small size. Thus in all cases the possession of c_t is a normal property of the assembly. These results can be readily extended to cases where there is an external field of force acting on the molecules.

By means of this assembly we can establish the meaning of ϑ in terms of T, by observing that the gas itself constitutes a constant volume gas thermometer. It is easy to show that the pressure of a gas must be $\frac{2}{3}$ of the mean kinetic energy

in unit volume, that is to say, $p = \mathrm{P}/\mathrm{V} \log(1/\vartheta)$. Since the gas temperature is measured by the relation $p\mathrm{V} = \mathrm{P}k\mathrm{T}$, we are again led to the relation $\vartheta = e^{-1/kT}$.

We may observe that it is now possible to drop the assumption of commensurability, which was necessary in the sections which dealt with quantized systems. It was there essential, physically speaking, in order that it should be possible that the whole of the energy should be held somewhere; but as we now have molecules which can hold energy in any amounts, it may be dispensed with, the modification being justified on the same assumptions and by the same sort of limiting process as have been used in this section. Again, we can see that the correct results are obtained if $\mathrm{H}(z)$ replaces $h(z)$ in (12·2) and all the other integrals, even though the interpretation as coefficient in a power series is no longer possible, and though the integrand is no longer single valued. In such many-valued integrands the limiting process shows that we simply require to take that value which is real on the positive side of the real axis.

§ 13. *The Maxwell Distribution Law.*

We have carried out the whole process so far with quantized systems included in the assembly, but it may be observed that it is immediately applicable to an assembly composed solely of molecules. If this is done the value of c_t in (12·51) establishes at once the Maxwell distribution law, and its fluctuation in (12·55) proves that it is a normal property of the assembly. This is probably the simplest complete proof of the ordinary distribution law; its special advantage is that by means of the fluctuations it is easily established that the actual distribution will hardly ever be far from the average.

The method can also be made to establish the distribution law for a mixture of gases *, and indeed for a mixture of any kind, provided that the systems can be considered to have separate energies.

It is also possible to extend the method to cases in which the total momentum or angular momentum is conserved, by constructing partition functions in more than one independent variable. In fact, there will be as many independent variables as there are uniform integrals of the dynamical equations of the assembly. For simplicity we shall suppose that the linear momentum in a given direction is conserved,

* The effects of the semi-permeable membranes of thermodynamics can be conveniently treated by the partition function.

and let its total amount be G. The method now requires the averaging process to be applied to expressions depending on

$$\frac{\mathrm{P}!}{c_1!\,c_2!\ldots}\delta_1^{c_1}\delta_2^{c_2},$$

where we now have not only

$$\Sigma_t c_t = \mathrm{P},\ \Sigma_t c_t \zeta_t = \mathrm{E},$$

but also

$$\Sigma_t c_t \mu_t = \mathrm{G},$$

where μ_t is the momentum in the given direction of a molecule in the tth cell. To sum the appropriate expressions we must take as our partition function

$$h(z,\ x) = \Sigma_t \delta_t z^{\zeta_t} x^{\mu_t}.$$

With this function C will be the coefficient of $z^{\mathrm{E}}x^{\mathrm{G}}$ in $[h(z, x)]^{\mathrm{P}}$, and this can be expressed as a double contour integral. So can the other averages, and the usual asymptotic expansions can be found. The correct distribution law follows on replacing $h(z, x)$ by the integral which is its limit when the sizes of the cells tend to zero. This subject lies rather outside the theme of the present paper and need not be elaborated further.

§ 16. *Summary.*

The whole paper is concerned with a method of calculating partitions of energy by replacing the usual calculation, which obtains the *most probable* state, and is mathematically unsatisfactory, by a calculation of the *average* state, which is the quantity that is actually required and which can be found with rigour by the use of the multinomial theorem together with a certain theorem in complex variable theory.

After a review of principles and two preliminary examples the real point of the method is illustrated in § 5. Here there are two groups of interacting Planck vibrators of different types. It is shown that the partition can be found by evaluating the coefficient of a certain power of z in an expression which is the product of power series in z. This coefficient can be expressed as a contour integral and can be evaluated by a well-known method, the "method of steepest descents." The result expresses itself naturally in terms of a parameter ϑ which is identified with temperature measured on a scale given by $\vartheta = e^{-1/k\mathrm{T}}$.

The work is extended to cover the partition among more

general quantized systems in §9, and examples are given. In §12 it is shown how it may be made to deal with assemblies composed partly of free molecules and partly of quantized systems. In §13 we deal with extensions possible when only molecules are present.

The methods we have described can also be made to throw an interesting light on the statistical foundations of thermodynamics; but in that connexion many points have arisen which require rather careful discussion, and in order not to make the present paper too long, we have deferred them to a future communication.

Cambridge,
May, 1922.

XLV. *The Heterodyne Beat Method and some Applications to Physical Measurements.* *By* MAURICE H. BELZ, *M.Sc. (Cantab.), Barker Graduate Scholar of the University of Sydney* *.

IN a recent paper †, a preliminary account was given of the application of the heterodyne beat method to the measurement of magnetic susceptibilities. In virtue of the importance of the method as a sensitive measure of physical quantities, it seems desirable to give a more complete account of the principle and of some of the difficulties encountered in its application.

Essentially the method consists of the following arrangement shown in fig. 1.

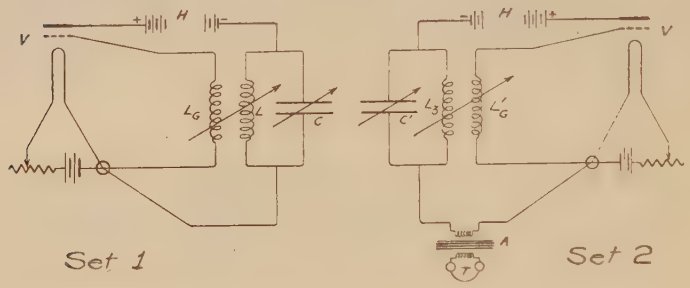
Two oscillating circuits, Set 1 and Set 2, are set up side by side and arranged so as to have approximately the same frequency. The two sets are loosely coupled so that in the telephone included in one of the circuits a resultant beat frequency is maintained equal to the difference between the frequencies of the fundamentals or overtones in the two circuits. If symmetry in the two circuits is essential, direct coupling can be replaced by indirect coupling by means of a third circuit in which the telephone is placed. In either case, when the beat frequency is low enough, an audible note will be heard in the telephone, and any changes in the constants of either circuit will cause the frequency of the audible note to alter by an amount equal to the change in frequency of the responsible circuit. This at once provides

* Communicated by Professor Sir E. Rutherford, F.R.S.

† Belz, Proc. Camb. Phil. Soc. vol. xxi. part 2 (1922).

a very sensitive method. It is now easily possible to maintain oscillations of frequencies up to 10^7 per second. Taking the case when Set 1 has a frequency of 1,000,000 per second, Set 2 a frequency of 1,001,000 per second, the audible note will have a frequency of 1,000 per second. If the frequency of Set 1 is changed to 1,000,001 per second, the frequency of the audible note will now be 999 per second, and this change in pitch can readily be observed by comparison with a note of standard pitch.

Fig. 1.



This sensitive method has been successfully employed by Herweg *, Whiddington †, Pungs and Preuner ‡, Falckenburg §, and several others in physical researches, but the precautions necessary for steadiness in the beat note have never been completely specified.

Precautions.

With high frequency oscillations of the order 3×10^5 per second to 5×10^5 per second such as were used in the present investigations, electrostatic shielding from all external influence was of the first importance. This was ensured by placing all the elements of the circuits in earthed metal-lined boxes, one of the variable capacities, by means of which final small adjustments were made, being provided with a long ebonite spindle which projected beyond the containing box. With the box closed the note from the telephone T was considerably reduced in intensity, and in order to obtain the maximum loudness, a small section was removed from the box, shielding being maintained by means of a piece of fine metal gauze.

* Herweg, *Zeit. f. Phys.* vol. iii. p. 36 (1920).
† Whiddington, Phil. Mag. vol. xi. p. 634 (1920).
‡ Pungs and Preuner, *Phys. Zeit.* vol. xx. p. 543 (1919).
§ Falckenburg, *Ann. d. Phys.* vol. lxi. 2, p. 167 (1920).

Solidity of foundation is a most important requirement. In the experiments of Whiddington *, although the apparatus was set up on a solid base, vibrations of the building even at 2 A.M. proved troublesome. A somewhat similar trouble was experienced in some of the earlier experiments when the apparatus was installed on the top floor of the laboratory. It was found that the vibration of the building caused by people walking about the corridors, and by the passage of heavy motor traffic, appreciably affected the steadiness of the note. Although some of the work was done during the night and over the week end, the trouble always persisted.

Finally the apparatus was transferred to a room on the ground floor and supported on stone pillars by means of solid rubber pads. The trouble was now completely removed so that successful observations could be made during the day despite the fact that people were continually walking beside the apparatus.

After lighting the valves, a certain amount of time must elapse before the oscillating system has settled down to a steady state. This initial variation is due to the heating and expansion of the elements of the valves, causing changes in the whole capacity linked with the oscillating systems. In order to save time, thus sparing the high tension batteries and prolonging the life of the valves, the latter were contained in small tin boxes, placed outside the large box, which were lagged with asbestos and cotton-wool. In this way the heat conduction was minimized, and the valves settled down much more rapidly. Other conditions being the same, it was found that certain valves were less satisfactory than others. For some types the settling down process was very long, and by the time the valve was set, other things began to vary. After long trials with "R," "Fotos," and "A. T." types, it was found that "B" type valves manufactured by the General Electric Company gave most satisfactory results, settling down most rapidly and remaining steadiest.

The effects of the changes in the elements of an oscillating system on the frequency have been examined by Eccles and Vincent † in the case of wave-lengths of 3000 metres. They determined that between certain limits for each value of the coupling between the plate and grid coils there was a particular value of the filament current for which the wave-length was a maximum. Working at this value of the current it was found possible to hold the beat note steady to

* Whiddington, *loc. cit.*

† Eccles and Vincent, Proc. Roy. Soc. A. vol. xcvi. p. 455 (1919).

one part in 100,000 for several minutes in spite of small unavoidable variations. With the frequencies employed in the present experiments, however, such a condition could not be established. The heating of the valve parts and the consequent change in capacity in the system resulting from changes in the filament current cause changes in wave-length which certainly far outweigh any real change due to increased thermionic emission alone. In order then to secure a constant filament current, accumulators of 100 ampere-hours capacity were employed. These were charged regularly after about three days' use, and after the valve had settled down, the current from them showed no variation during a single run.

Faulty contacts of wires joining the elements of the circuits were avoided by soldering, the only sources of uncertainty being the sliding resistances in the filament circuits. These, however, were good types with bright surfaces and stiff springs so that the chance of error due to change of contact was small.

The principal cause of variation in the frequencies of the circuits was found to be due to variations in the high tension batteries. This trouble has been mentioned by Eccles and Vincent *. In the present work the plate voltage was obtained from trays of portable accumulators of fairly low capacity, each tray providing 40 volts. After the valves had been burning for an hour or so, taking a current of about 10 milliamperes, this voltage began to vary and the beat note consequently drifted. However, giving the valves time to settle down, a matter of 15 to 20 minutes, it was found possible to hold the heterodyne note quite steady for intervals of 30 to 60 seconds, and this is ample time in which to make a single observation. After about 90 minutes burning the variation was too rapid and the batteries had to be recharged. The size and consequent capacity of the cells of these batteries is limited by the fact that they have to be contained in a metal box, and thus this source of variation can only be provided for in special cases.

Technique.

It is essential to maintain the oscillations generated in the circuits at frequencies considerably different from the natural frequencies of the coils alone †, that is to say with an appreciable capacity in the system, and under these conditions the frequency, n, of the oscillations in such a circuit containing

* Eccles and Vincent, *loc. cit.*

† *Cf.* Townsend, Phil. Mag. vol. xlii. August (1921).

inductance L and capacity C, is given very approximately by

$$n = 1/(2\pi\sqrt{LC}).$$

Changes in n can thus be brought about by changes in C or L. In the experiments to be described below, the changes in n were brought about by variations in L, and in this case, with C constant, a small variation, dL, in the inductance produces a corresponding change, dn, in the frequency given by

$$dn/n = \tfrac{1}{2}d\mathrm{L}/\mathrm{L}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

The experimental part thus reduces itself to a determination of dn. This is accomplished by obtaining beats between the heterodyne note and a note of constant pitch, and then counting the change in the number of beats per second caused by the change in inductance. A considerable amount of practice in listening is required in order readily to be able to adjust the heterodyne note to the pitch of the constant note. This note can be very conveniently obtained by means of a third set, some distance away from the other sets, oscillating with audible frequency, in the plate circuit of which a telephone is placed. The intensity of the note heard can be altered by adjusting the filament current, and in this respect the note is very much more convenient than that obtained from a tuning-fork. For it was found that the heterodyne note could be more easily brought to tune with the standard note, and false beats more readily recognized when this latter could be altered so that both notes had approximately the same intensity.

In some of the experiments * it was found impossible to obtain a beat note of convenient audible frequency when the fundamental frequencies of the oscillations were approximately the same. It was observed that, as the capacity of one of the sets was altered, only very shrill notes could be heard on either side of the very large region of silence. This synchronization effect appears to depend on several factors, but chiefly on the coupling between the circuits. On account of the limited size of the box containing the coils, the coupling could not be reduced beyond a certain lower limit, and reducing the strengths of the oscillatory currents merely reduced the intensity of the limited note. In all these cases it was possible to obtain the heterodyne note between the fundamental of Set 2 and the first overtone of Set 1, which was quite steady and possessed the normal region of silence. Since the changes in n were produced by

* Those in which the determinations of the magnetic susceptibilities of certain salts were made, see below.

variations in the inductance of Set 1, this arrangement increases the sensitiveness of the method. For let N be the frequency, determined at the centre of the region of silence, of the fundamental oscillation in Set 2, n the frequency of the fundamental oscillation in Set 1, then since the first overtone of Set 1 is employed to produce the note, $N=2n$. Let the frequency of the audible note from the third circuit be m. Then when the heterodyne note is adjusted, by slightly varying the capacity of Set 2, so that q beats per second are counted, the frequency of Set 2 is $(N\pm m\pm q)$ $=(2n\pm m\pm q)$. If now the frequency of the fundamental oscillation of Set 1 is altered by dn per second, the frequency of the first overtone is altered by an amount $2dn$ per second, so that the frequency of the heterodyne note is now $(2n\pm m\pm q)-(2n\pm 2dn)=(m\pm q\pm 2dn)$, whence if a change of p beats per second is observed when the inductance change is accomplished, $p=2dn$. The sensitiveness is thus doubled, and could similarly be increased by employing higher overtones of Set 1. Against this, however, is the fact that the notes so obtained are very feeble, and counting becomes increasingly difficult.

From equation (i.) we see that the sensitiveness depends on n. It is now possible to maintain oscillations of frequencies up to 10^7 per second, but in cases where the change in inductance is caused by inserting a specimen within the coil, there is an upper limit to n determined by the form and function of the coil L. It is necessary to divide this coil into two parts between which there is no mutual inductance, one part L_1 being coupled to the grid circuit in order to maintain the oscillations, the other part L_2 serving as the coil in which the inductance changes occur. This latter part must be a fairly long coil in order that there may be an appreciable region within it through which the magnetic field is constant, in which region the specimen is placed. On account of the dimensions of this coil, the first part has to possess a fairly large inductance in order to get sufficient mutual inductance with the grid coil: further, a certain amount of coupling is required with Set 2 to produce the heterodyne note.

Experimental.

In the present experimental arrangements the details of the coils are as follows:—

Coil L_1.

The coil was 10 cm. long, and consisted of 100 turns of copper wire, no. 22 s.w.g., double cotton covered. It was

wound on a short length of glass tubing and had an effective diameter of 2·10 cm. The self-inductance, employing the exact formula of Nagaoka *, viz.,

$$L_s = 4\pi^2 a^2 n_1^2 \, b \, . \, K,$$

where L_s is the self-inductance of a current sheet of the same dimensions as the coil, n_1 the number of turns per cm., a the effective radius, b the total length, and K a factor depending on the ratio of the diameter of the coil to the length, to which was applied the correction for spacing, was calculated to be 39,160 cm. The small frequency correction was neglected.

Coil L_2.

The coil was 36·70 cm. long, and consisted of 541 turns of copper wire, no. 24 s.w.g., silk covered. It was wound on a long glass tube, of external diameter 1·00 cm., and separated therefrom by means of a layer of paraffined paper. The effective diameter ($2a$) of the coil was 1·105 cm., and self-inductance, calculated as above, was 92,430 cm.

The total inductance L ($= L_1 + L_2$) is thus 131,600 cm.

The coil L_2 was outside the box containing the rest of the circuits, and was shielded from external electrostatic influences by means of an enveloping earthed metal cylinder.

Coil L_3.

The length was 9 cm., and the coil consisted of 90 turns of copper wire, no. 22 s.w.g., double cotton covered. It was wound on a short length of glass tubing and had an effective diameter 4·13 cm. The self-inductance was similarly calculated to be 124,600 cm.

The capacities employed had a range of 100 to 1200 microfarads and were provided with a slow movement.

Changes in the frequency of the oscillations of Set 1 brought about by the insertion of a specimen within the coil L_2 may be due to three causes :—

(a) In the first place, if the coil is not shielded from the electrostatic effect of the specimen, the self capacity of the coil will be changed. In order to observe changes of inductance alone, it is necessary to guard against this possibility. This was done by depositing a thin layer of platinum † on the outside of the glass tube on which the coil L was wound, and earthing. The thickness of the deposit, obtained by weighing, was 7×10^{-6} cm. It is necessary to

* Nagaoka, Jour. Coll. Sci. Tokyo, xxvii. art. 6, p. 18 (1909).

† The function of the paraffined paper was to prevent any possible short-circuiting of the coil through the layer of platinum.

determine the effect of this shield on the strength of the magnetic field within. The magnetic force, H_t, at a depth t in a mass of metal is related to the force, H_0, at the surface by the equation

$$H_t = H_0 e^{-\sqrt{\frac{2\pi\mu\rho t}{\sigma}}},$$

in which μ, σ represent the permeability and specific resistance respectively of the metal, and $\rho = 2\pi n$, n being the frequency. Taking $n = 4{\cdot}84 \times 10^5$ per second, the largest frequency used, and for platinum, $\mu = 1$, $\sigma = 11{,}000$ c.g.s. e.m.u., we find that within the shield for $t = 7 \times 10^{-6}$ cm.,

$$H_t/H_0 = e^{-0\,000292},$$
$$= 0{\cdot}9997.$$

The effect of the field on the changes of inductance can thus be neglected.

With the shield, the remaining causes of the change of frequency are due entirely to changes of inductance, being

(*b*) an eddy current effect within the specimen, and

(*c*) in the case of the magnetic substances, a susceptibility effect.

The Eddy Current Effect.

The magnetic field, H, within the coil will be of a harmonic type, and on this account circular eddy currents will be induced in the specimen in planes perpendicular to the axis of the coil and in such a direction that the magnetic forces arising from them oppose and consequently diminish the value of H. This virtually means a diminution in the inductance of the coil, and the frequency change will be in the direction of n increasing. This result can also be predicted mathematically by regarding the specimen as equivalent to a coil with self-inductance and resistance, coupled to the main coil. The analysis, however, is complicated and its development was not proceeded with. Some experiments were made, however, to determine the order of the change in inductance and its dependence on the characteristics of the specimen.

In the first place, as bearing on the results obtained in the magnetic measurements, sulphuric acid was examined. This was contained in a long glass tube, the effect of which had previously been determined to be zero, and was lowered into the oscillating coil L_2. Any change in inductance due to an eddy current effect should certainly depend on the

conductivity of the specimen. This solution had a conductivity far greater than any of the magnetic specimens, which were examined in liquid, crystal, and powder forms, but, counting over periods ranging beyond ten seconds, no variation in the beat note was observed. Accordingly it was assumed that the effect in the magnetic substances was negligible.

Some tests were then made with different lengths and sizes of graphite taken from ordinary pencils. The conductivities of these specimens were much greater than that of the solution of acid, but there were no changes in the beat note indicating an increase of frequency. In the case of some specimens changes occurred which corresponded to an increase of inductance, but some iron must have been present in them.

Finally, some tests were made on different specimens of copper, brass, manganin, platinoid, and constantan wires. In these experiments, which were carried out after the susceptibility determinations, some alterations in the elements of the circuits enabled the heterodyne note to be obtained by beats produced between the fundamental oscillations.

It is interesting, at this stage, to give the results obtained for the variation in frequency change with the conductivities of the specimens. In this connexion two tests were made, the first employing small specimens and counting the beats, the second employing large specimens and computing the frequency change from the alteration in capacity necessary to bring the heterodyne note to coincidence with the auxiliary note.

(*a*) The specimens used were wires of copper, brass, platinoid, and manganin, each of length 0·32 cm., and diameter 0·711 mm. The wave-length was 710 metres. The results are included in Table I.

TABLE I.

Specimen.	Frequency Change per second. *dn.*
Copper	9·54
Brass	4·88
Platinoid	0·33
Manganin	0·28

(*b*) The specimens used were wires of copper, brass, and constantan, each of length 8 cm. and diameter 2·03 mm.

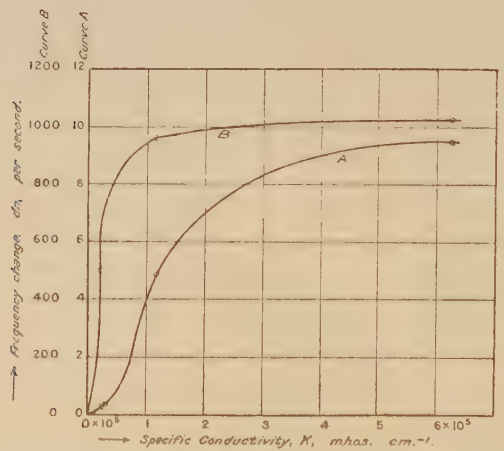
The wave-length was 725 metres. The results are included in Table II.

TABLE II.

Specimen.	Capacity Change (arbitrary units).	Frequency Change per second. *dn.*
Copper	201	1027
Brass	190	961
Constantan	98	501

The wires of platinoid, manganin, and constantan used in the above tests contained 15 per cent., 4 per cent., and 40 per cent. nickel respectively. The magnetic susceptibilities of copper-nickel alloys have been determined by Gans and Forseca *, who found that when the nickel content was 40·4 per cent. the susceptibility was only $0{\cdot}189 \times 10^{-6}$ c.g.s., being much smaller for lower percentages. The effect of the susceptibilities of the specimens used on the frequency changes can thus be neglected.

Fig. 2.



The specific conductivities, K, in mhos cm^{-1}., of the materials used, taken, with the exception of brass, from Kaye and Laby's tables, are :—for copper, $K = 6{\cdot}29 \times 10^5$, for platinoid, $K = 0{\cdot}291 \times 10^5$, for manganin, $K = 0{\cdot}233 \times 10^5$, and for constantan, $K = 0{\cdot}204 \times 10^5$. The specific conductivity for the brass used was determined to be $K = 1{\cdot}182 \times 10^5$.

Fig. 2 represents the relations obtained by plotting *dn* against K, curve (*a*) referring to test (*a*), curve (*b*) to test (*b*).

* Gans u. Forseca, *Ann. d. Phys.* vol. lxi. p. 742 (1920).

The forms of both curves indicate a relation of the type

$$dL = \text{constant} \times \frac{K^2}{K^2 + B},$$

the term B varying for different sizes of specimen, being relatively less important the greater the whole conductivity of the specimen, as shown in curve (*b*). A similar type of dependence was calculated by Mr. Kapitza, of the Cavendish Laboratory, for the case of a thin spherical shell.

For solid cylinders, the dependence of the frequency change on other characteristics of the specimens was examined, but it is hoped to give a complete account of the results together with further tests on different forms of specimens, in a subsequent paper.

The Application of the Method to the Determination of the Magnetic Susceptibilities of certain Salts.

The general principle of the method has been given in the previous paper *. It has since been applied to the determination of the magnetic susceptibilities of many salts, the results obtained being given below. In addition it seems desirable to indicate more carefully the nature and magnitude of the corrections to be applied.

Considering the insertion of a magnetic substance in the form of a cylinder of cross section A′ and length *l*′, the volume susceptibility of which is K_v, within the coil L of Set 1, the cross section and length of which are A and *l* respectively, thus causing the frequency, *n*, of the oscillations to alter by an amount *dn*, we find, subject to the corrections to be given below,

$$K_v = \frac{1}{2\pi} \cdot \frac{dn}{n} \cdot \frac{Al}{A'l'} \cdot \frac{L_1 + L_2}{L_2}.$$

In all the experiments for determining K_v, the heterodyne note was obtained by beats between the first overtone of the oscillations in Set 1 and the fundamental oscillation of Set 2, as already mentioned on pages 483, 484 *suprà*. In this case, if N is the frequency of the oscillations in Set 2, and a change of *p* beats per second is observed on inserting the specimen, $N = 2n$, and $p = 2dn$. We thus obtain

$$K_v = \frac{1}{2\pi} \cdot \frac{p}{N} \cdot \frac{Al}{A'l'} \cdot \frac{L_1 + L_2}{L_2} \quad . \quad . \quad . \quad . \quad \text{(ii.)}$$

* Belz, *loc. cit.*

Before this formula can be applied it is necessary to investigate several corrections. The absorption in the platinum shield which covered the tube on which L_2 was wound, and the eddy current effect, have been discussed and shown to produce no correction terms. But there remain two further corrections to be investigated, (i.) due to the demagnetizing effect of the specimen, and (ii.) due to the end correction term in the calculation of the self-inductance of the coil and the effect on this due to the position of the specimen.

(i.) The demagnetizing effect on the magnetic field due to the magnetism induced in the specimen.

By treating the specimen as an elongated ellipsoid of revolution, of semi-minor and semi-major axes a and c respectively, with its long axis parallel to the field, Ewing * has shown that if H is the value of the magnetic force within the specimen, and H′ the original value of the magnetic force before the specimen was inserted, then

$$H = H'(1 - NK_v),$$

where N is given by

$$N = 4\pi(1/e^2 - 1)\left\{\frac{1}{2e}.\log_\epsilon(1+e)/(1-e) - 1\right\},$$

e being the eccentricity and equal to $\sqrt{1-a^2/c^2}$.

In a typical case, that of cobalt chloride in solution, which had a value of K_v approximately 20×10^{-6} c.g.s., $2a = 0{\cdot}507$ c.m., $2c = 8{\cdot}0$ c.m. Hence $e = 0{\cdot}998$. This gives $N = 0{\cdot}126$, and hence

$$H = H'(1 - 0{\cdot}126 \times 20 \times 10^{-6})$$
$$= H'(1 - 2{\cdot}52 \times 10^{-6}),$$

so that this correction is negligible.

To get the effect on the external field, consider the resultant magnetism induced on the ends and sides of the specimen. Ewing † shows that the free magnetism, although densest at the ends, extends towards the middle, and it is only on the equatorial line that there is none. Also the total quantity of free magnetism on any narrow zone taken perpendicular to the direction of magnetization

* Ewing, 'Magnetic Induction in Iron and other Metals,' pp. 23–25.
† Ewing, *loc. cit.* pp. 25–27.

is proportional to the width of the zone and to its distance from the equatorial line.

Consider such a zone at distance x from the equatorial line, x being measured in the positive direction of the field, width dx. Then the total quantity of free magnetism on it is equal to $+Cxdx$, where C is determined from the fact that the total quantity of positive (or negative) magnetism, *i. e.* $\int_0^c Cxdx$, is equal to $\pi a^2 I$, I being the intensity of magnetization. This gives $C=2\pi\frac{a^2}{c^2}I$, and hence the free magnetism on the strip is $+2\pi\frac{a^2}{c^2}I.xdx$.

Let us consider the effect of this quantity of positive magnetism at the distance x, and an equal quantity of negative magnetism at $-x$ at a point on the equatorial plane outside the specimen. Suppose the free magnetism on the strip to act in regard to external points, as if it were concentrated at its centre of gravity, and let d be the distance of the point in question from the axis of the specimen. Then the magnetic force in a direction parallel to the axis at the point 0, d will be

$$-4\pi\frac{a^2}{c^2}I.\frac{xdx}{x^2+d^2}.\frac{x}{\sqrt{x^2+d^2}},$$

and the effect due to the whole specimen will be the integral of this from 0 to c, which becomes

$$-4\pi\frac{a^2}{c^2}I.\left(-\frac{c}{\sqrt{c^2+d^2}}+\sinh^{-1}\frac{c}{d}\right).$$

If H is the value of the magnetic force within the specimen, which we have seen is also the original value of the field within the coil before the specimen was inserted, we may write $I=K_vH$, and the field at the point 0, d is reduced from H to

$$H\left\{1-4\pi\frac{a^2}{c^2}K_v\left(-\frac{c}{\sqrt{c^2+d^2}}+\sinh^{-1}\frac{c}{d}\right)\right\}.$$

Taking $d=0{\cdot}5$ cm., *i. e.* just within the winding of the coil, and with the same numerical data as before, this becomes

$$H(1-1{\cdot}79\times10^{-6}).$$

At a point on the surface of the specimen, for $d=0{\cdot}25$ cm. we obtain for the reduced field,

$$H(1-2{\cdot}5\times10^{-6}).$$

The correction in this case is also negligible, and we are

thus justified in completely neglecting the effects of demagnetization.

(ii.) The effect of the end correction term and the position of the specimen.

In a long coil there is an appreciable length over which the magnetic force is constant and given by $H=4\pi n_1 i$, n_1 being the number of turns per unit length. At the ends the force falls to half value, and this diminution in H is responsible for the correction term K in Nagaoka's formula

$$L=4\pi^2 a^2 n_1^2 b \,.\, K.$$

When this correction is small and so can be neglected, the expression (ii.) becomes exact. In the present case, the value of K was equal to 0·9873 and the error involved in neglecting this end correction is about 1·3 per cent. We can allow for the correction in the following way:

The short specimen (about 8 cm. as compared with the length of the coil, 36·70 cm.) was suspended in approximately the centre of the coil, which can thus be supposed to consist of three coils in series, one in the centre of length equal to that of the specimen and without end correction, and two approximately equal coils on either side, to the open ends of which the correction is to be applied. Let l' be the length of the specimen, l the length of the coil, then the total self-inductance is $L=Cl/K$, while the self-inductance of the coil of length l' is $L_0=Cl'$, where $C=4\pi^2 a^2 n_1^2$. The area of cross section of the coil being A, that of the specimen A', the self-inductance of this portion is altered to L_0' where

$$L_0'=L_0(1+4\pi K_v A'/A),$$

so that the whole change in inductance of the coil, dL, is given by

$$\begin{aligned} dL &= L_0 4\pi K_v A'/A, \\ &= L_0 4\pi K_v A' l'/(Al K), \end{aligned}$$

and thus the expression (ii.) in the corrected form becomes

$$K_v=\frac{1}{2\pi}\cdot\frac{p}{N}\cdot\frac{K\,.\,\text{volume of coil}}{\text{volume of specimen}}\cdot\frac{L_1+L_2}{L_2}. \quad . \quad \text{(iii.)}$$

Experimental Errors.

The accuracy of the estimations depends almost entirely on the determinations of the change in the number of beats per second and of the frequencies. The counting was done by means of a stop-watch guaranteed to read tenths of a second. The heterodyne note was adjusted by means of the fine movement on the condenser of Set 2 so that a reasonable

number of beats per second, sometimes zero, was heard. The time for 20 beats was noted, the specimen then inserted the new time for 20 beats being again observed, and finally a third count made when the specimen was removed. The note was then slightly varied and the same procedure repeated. In this way from 6 to 10 readings were obtained for each particular frequency used. A review of all the measurements so made under conditions when the heterodyne note was steady show that the greatest error incurred was about 2·2 per cent.

The wave-lengths were measured with a calibrated Townsend wave-meter, and the resonance point could be fixed to within 2 metres. The shortest wave-length measured was about 350 metres corresponding to a fundamental oscillation in Set 2, so that the maximum error involved here is about 0·6 per cent.

From all sources, then, the maximum error involved in the estimation of the susceptibilities is about 3 per cent.

The Experimental Results.

The specimens were all prepared by Kahlbaum, Berlin, and were contained in short lengths of glass tubing thus permitting of quick insertion into the coil. The effect of the tubing alone was found to be zero in every case. The results are given below.

I. *Ferric Chloride.*—The salt was examined in the form of a solution in air-free water. It was contained in a closed glass tube, occupied a volume 1·321 c.c., and had an approximate length 7·5 cm. The density was determined to be 1·152 gm. per c.c. at 15° C., and a volumetric estimation showed that the solution contained 0·189 gm. $FeCl_3$ per c.c. The observations are shown in Table III.

TABLE III.

Wave-length of Set 2 in metres.	Frequency of Set 2 per sec. N.	Frequency of Set 1 per sec. $n=\frac{1}{2}N$.	Change in number of beats per sec. $p=2dn$.	p/N.	Temperature degrees C.
	$\times 10^5$	$\times 10^5$		$\times 10^{-6}$	
372	8·07	4·03	2·59	3·21	15
385	7·80	3·90	2·49	3·19	15
400	7·50	3·75	2·39	3·19	15
418	7·18	3·59	2·29	3·19	15

Mean $p/N=3·19\times 10^{-6}$ at 15° C.

The values of p/N show that for the range of frequencies used the susceptibility is constant. This was found to be the case for all the substances examined.

Formula (iii.) gives

$$K_v = \frac{1}{2\pi} \times 3{\cdot}19 \times 10^{-6} \times \frac{(\pi/4)(1{\cdot}105)^2 \times 36{\cdot}70 \times 0{\cdot}9873}{1{\cdot}321} \times \frac{131600}{92430}$$

$$= 19{\cdot}1 \times 10^{-6} \text{ c.g.s.}$$

The mass susceptibility of the solution K_{m_1} is thus

$$K_{m_1} = 19{\cdot}1 \times 10^{-6}/1{\cdot}152$$
$$= 16{\cdot}53 \times 10^{-6} \text{ c.g.s.}$$

For a solution of a salt in water, the mass susceptibility is given by

$$K_{m_1} = p_0 K_m + (1 - p_0) K_{m_0},$$

where p_0 = mass of salt per c.c.,

K_m = mass susceptibility of the water-free salt,

K_{m_0} = susceptibility of water, which may be taken as $-0{\cdot}75 \times 10^{-6}$ c.g.s.

We thus obtain

$$K_m = 90{\cdot}7 \times 10^{-6} \text{ c.g.s. at } 15^\circ \text{ C.}$$

The values for K_m determined previously by balance methods are* 92×10^{-6}, 91×10^{-6}, 83×10^{-6}, 92×10^{-6}, 88×10^{-6}, and 103×10^{-6} c.g.s. with a mean value 91×10^{-6} c.g.s. The present result is in good agreement, and thus shows that up to a frequency of $4{\cdot}03 \times 10^5$ per second the susceptibility is not altered.

II. *Ferrous Sulphate.*—Tests were made on the salt in forms of crystals and powder. The crystals were good ones of the monoclinic type, and on estimation proved to have the composition, $FeSO_4, 7H_2O$ almost exactly. Equal masses of crystals and powder were used, the powder being obtained by grinding up the crystals in a glass mortar. The substances were enclosed in glass tubes, the transference after weighing being rapid to avoid absorption of water from the atmosphere. The mass of each specimen was 1·00 gm. at 15° C. At this temperature the density of $FeSO_4, 7H_2O$ crystals is 1·899 gm. per c.c., and hence the volume of each specimen was 0·527 c.c. In the form of powder this volume occupied a length 5·6 cm., while for the crystals the length was about 8 cm.

* Landolt and Börnstein *Tabellen* (1912).

The observations are shown in Table IV.

TABLE IV.

Wave-length of Set 2 in metres.	Frequency of Set 2 per sec. N.	Frequency of Set 1 per sec. $n=N/2$.	Change in number of beats per sec. $p=2dn$.		p/N.		Temperature degrees C.
			Cryst.	Powder.	Cryst.	Powder.	
	$\times10^5$	$\times10^5$			$\times10^{-6}$	$\times10^{-6}$	
352	8·53	4·26	4·40	4·40	5·15	5·15	16
375	8·00	4·00	4·10	4·12	5·13	5·15	16
392	7·65	3·83	3·91	3·90	5·11	5·10	16
410	7·32	3·66	3·74	3·71	5·11	5·07	16
414	7·25	3·63	3·70	3·69	5·10	5·09	16
417	7·20	3·60	3·68	3·68	5·11	5·11	16

Mean p/N for both crystals and powder $=5·12\times10^{-6}$ at 16° C.

The susceptibility of the salt is thus the same in the solid as in the powder form. A similar identity in the susceptibilities of different forms of the same material was observed by Wilson * using a balance method in the investigation of certain iron ores.

The volume susceptibility is

$$K_v=76·6\times10^{-6}\text{ c.g.s.},$$

whence the mass susceptibility of the complete salt is $40·4\times10^{-6}$ c.g.s. The percentage mass of $FeSO_4$ in one gram of salt is 54·6, so that, neglecting the contribution to the susceptibility of the water of crystallization, we find

$$K_m=74·0\times10^{-6}\text{ c.g.s. at }16°\text{ C.}$$

The mean of the values for K_m, all determined in the form of a solution, given in the *Tabellen* of Landolt and Börnstein is 78×10^{-6} c.g.s. Finke† found for K_m for the complete salt a value 80×10^{-6} c.g.s., and the present result agrees very well with these.

III. *Ferrous Ammonium Sulphate.*—The salt was examined in the form of monoclinic crystals which proved, on estimation, to have the composition $FeSO_4(NH_4)_2SO_4$, $6H_2O$ to an accuracy of 0·3 per cent. The density of this salt is 1·813 gm. per c.c. at 15° C. A mass of 1 gm. was taken and placed in a glass tube, occupying a length of about 8 cm.,

* Wilson, Proc. Roy. Soc. A. vol. xcvi. p. 429 (1919).
† Finke, *Ann. d. Phys.* (4) xxxi. p. 149 (1910).

and a volume 0·551 c.c. The observations are shown in Table V.

TABLE V.

Wave-length of Set 2 in metres.	Frequency of Set 2. N.	Frequency of Set 1. $n=N/2$.	Change in number of beats per sec. $p=2dn$.	p/N.	Temperature degrees C.
	$\times 10^5$	$\times 10^5$		$\times 10^{-6}$	
335	8·95	4·47	3·39	3·79	16
340	8·83	4·41	3·34	3·78	16
363	8·72	4·13	3·13	3·79	16
400	7·50	3·75	2·84	3·79	16

Mean $p/N=3·79\times10^{-6}$ at 16°C.

We find hence

$$K_v=54·0\times10^{-6} \text{ c.g.s..}$$

which gives for the mass susceptibility of the complete salt $29·8\times10^{-6}$ c.g.s. The percentage mass of $FeSO_4(NH_4)_2SO_4$ in one gram of salt is 72·5, and hence we obtain

$$K_m=41·1\times10^{-6} \text{ c.g.s. at } 16°C.$$

The values given in the *Tabellen* of Landolt and Börnstein of K_m for the salt when examined in the form of a solution at 18° C are 44×10^{-6}, and 45×10^{-6} c.g.s.

IV. *Nickel Chloride.*—The salt was examined in the form of a solution in air-free water. The volume of the specimen was 1·572 c.c. and occupied a length in the glass tube of approximately 7·4 cm. The density was determined to be 1·332 gm. per c.c., and an electrolytic estimation yielded 0·255 gm. $NiCl_2$ per c.c. The observations are shown in Table VI.

TABLE VI.

Wave-length of Set 2 in metres.	Frequency of Set 2. N.	Frequency of Set 1. $n=N/2$.	Change in number of beats per sec. $p=2dn$.	p/N.	Temperature degrees C.
	$\times 10^5$	$\times 10^5$		$\times 10^{-6}$	
355	8·45	4·22	2·12	2·51	15
380	7·90	3·95	1·99	2·52	15
404	7·43	3·71	1·88	2·52	15

Mean $p/N=2·52\times10^{-6}$ at 15° C.

This gives

$$K_v = 12{\cdot}62 \times 10^{-6} \text{ c.g.s.}$$

The mass susceptibility of the solution is

$$K_{m_1} = 9{\cdot}49 \times 10^{-6} \text{ c.g.s.},$$

and the mass susceptibility of the water-free salt becomes

$$K_m = 39{\cdot}5 \times 10^{-6} \text{ c.g.s. at } 15^\circ \text{ C.}$$

This is in good agreement with the values given in the *Tabellen* of Landolt and Börnstein, the mean of which is $39{\cdot}66 \times 10^{-6}$, but is considerably different from the value recently given by Théodoridès *, viz. $47{\cdot}6 \times 10^{-6}$ c.g.s. at 15°·2 C.

V. *Nickel Sulphate.*—The specimen was in the form of the green rhombic prism crystals which, on estimation, were shown to have the composition $NiSO_4$, $7H_2O$; the density of these crystals is (Thorpe and Watts) 1·950 gm. per c.c. A mass of 1·438 gm. occupying a volume 0·737 c.c. was used, having a length in the glass tube of approximately 7·2 cm. The observations are shown in Table VII.

TABLE VII.

Wave-length of Set 2 in metres.	Frequency of Set 2. N.	Frequency of Set 1. $n=N/2$.	Change in number of beats per sec. $p=2dn$.	p/N.	Temperature degrees C.
	$\times 10^5$	$\times 10^5$		$\times 10^{-6}$	
342	8·77	4·38	2·63	3·00	16
370	8·12	4·06	2·44	3·00	16
412	7·29	3·64	2·16	2·96	16

Mean $p/N = 2{\cdot}99 \times 10^{-6}$ at 16°C.

This gives

$$K_v = 32{\cdot}1 \times 10^{-6} \text{ c.g.s.},$$

from which we get the mass susceptibility of the complete salt to be $16{\cdot}43 \times 10^{-6}$ c.g.s. The percentage mass of $NiSO_4$ in one gram of salt is 55, and hence we obtain

$$K_m = 29{\cdot}9 \times 10^{-6} \text{ c.g.s. at } 16^\circ \text{ C.}$$

The mean of the values in the *Tabellen* is 30×10^{-6} c.g.s., while Finke † finds for K_v the value $29{\cdot}1 \times 10^{-6}$ c.g.s.

* Théodoridès, *Journ. d. Phys.* III. i. p. 1 (1922).

† Finke, *loc. cit.*

VI. *Cobalt Sulphate.*—Tests were made with the salt in the form of crystals and powder.

(*a*) Tests on crystals.

The salt proved on estimation to have the composition $CoSO_4, 7H_2O$; the density of this salt is 1·950 gm. per c.c. A mass of 1·1375 gm. was used which thus occupied a volume 0·583 c.c. The length of the crystal column was 6 cm. The observations are shown in Table VIII.

TABLE VIII.

Wave-length of Set 2 in metres.	Frequency of Set 2. N.	Frequency of Set 1. $n=N/2$.	Change in number of beats per sec. $p=2dn$.	p/N.	Temperature degrees C.
	$\times 10^5$	$\times 10^5$		$\times 10^{-6}$	
349	8·60	4·30	4·28	4·97	16
385	7·80	3·90	3·85	4·94	16
410	7·32	3·66	3·59	4·91	16

Mean $p/N=4·94\times10^{-6}$ at 16° C.

This gives

$$K_v=66·0\times10^{-6} \text{ c.g.s.},$$

and thus the mass susceptibility of the complete salt is $33·85\times10^{-6}$ c.g.s. We thus obtain

$$K_m=61·4\times10^{-6} \text{ c.g.s. at } 16° \text{ C.}$$

(*b*) Tests on powder.

A mass of 1·3150 gm. was used having a volume 0·674 c.c. and occupying a length in the glass tube 5·5 cm. The observations are shown in Table IX.

TABLE IX.

Wave-length of Set 2 in metres.	Frequency of Set 2. N.	Frequency of Set 1. $n=N/2$.	Change in number of beats per sec. $p=2dn$.	p/N.	Temperature degrees C.
	$\times 10^5$	$\times 10^5$		$\times 10^{-6}$	
350	8·57	4·28	4·88	5·70	16
385	7·80	3·90	4·45	5·71	16
414	7·25	3·62	4·14	5·72	16

Mean $p/N=5·71\times10^{-6}$ at 16° C.

This gives

$$K_v = 67{\cdot}0 \times 10^{-6} \text{ c.g.s.},$$

and finally

$$K_m = 62{\cdot}4 \times 10^{-6} \text{ c.g.s. at } 16^\circ \text{ C.}$$

The results of the two tests thus give as mean values

$$K_v = 66{\cdot}5 \times 10^{-6} \text{ c.g.s.},$$
$$K_m = 61{\cdot}9 \times 10^{-6} \text{ c.g.s. at } 16^\circ \text{ C.}$$

For the complete salt Finke * finds $K_v = 68 \times 10^{-6}$ c.g.s. The mean values for K_m in the *Tabellen* is 66×10^{-6} c.g.s., while Théodoridès † gives for K_m the value $64{\cdot}5 \times 10^{-6}$ c.g.s. at 16° C.

VII. *Cobalt Chloride.*—The salt was examined in the form of a solution in air-free water. It occupied a volume 1·620 c.c. and had a length in the glass tube 8 cm. The density was determined to be 1·186 gm. per c.c., and an electrolytic estimation yielded 0·2078 gm. $CoCl_2$ per c.c. The observations are shown in Table X.

TABLE X.

Wave-length of Set 2 in metres.	Frequency of Set 2. N.	Frequency of Set 1. $n = N/2$.	Change in number of beats per sec. $p = 2dn$.	p/N.	Temperature degrees C.
	$\times 10^5$	$\times 10^5$		$\times 10^{-6}$	
340	8·82	4·41	3·48	3·94	20
385	7·80	3·90	3·09	3·96	20
414	7·25	3·61	2·85	3·94	20

Mean $p/N = 3{\cdot}95 \times 10^{-6}$ at 20° C.

This gives

$$K_v = 19{\cdot}30 \times 10^{-6} \text{ c.g.s.},$$

from which we find for the mass susceptibility of the solution

$$K_{m_1} = 16{\cdot}28 \times 10^{-6} \text{ c.g.s.},$$

and finally for the mass susceptibility of the water-free salt

$$K_m = 81{\cdot}3 \times 10^{-6} \text{ c.g.s. at } 20^\circ \text{ C.}$$

* Finke, *loc. cit.*
† Théodoridès, *loc. cit.*

The values in the *Tabellen* for K_m are 81×10^{-6}, 101×10^{-6}, and 82×10^{-6} c.g.s., while Théodoridès* gives $97{\cdot}9 \times 10^{-6}$ c.g.s. The present result thus indicates that the lower values are the more accurate.

Summary of Results.

The results obtained are grouped together in Table XI.

TABLE XI.

Substance.	Form in which tested.	Mass susceptibility of water-free salt.	Temp. C.
Ferric Chloride, $FeCl_2$.	Solution	$90{\cdot}7 \times 10^{-6}$ c.g.s.	15°
Ferrous Sulphate, $FeSO_4,7H_2O$.	Crystals and Powder.	$74{\cdot}0 \times 10^{-6}$ c.g.s.	16°
Ferrous Ammonium Sulphate, $FeSO_4, (NH_4)_2 SO_4, 6H_2O$.	Crystals.....	$41{\cdot}1 \times 10^{-6}$ c.g.s.	16°
Nickel Chloride, $NiCl_2$.	Solution	$39{\cdot}5 \times 10^{-6}$ c.g.s.	15°
Nickel Sulphate, $NiSO_4,7H_2O$.	Crystals.....	$29{\cdot}9 \times 10^{-6}$ c.g.s.	16°
Cobalt Sulphate, $CoSO_4,7H_2O$.	Crystals and Powder.	$61{\cdot}9 \times 10^{-6}$ c.g.s.	16°
Cobalt Chloride, $CoCl_2$.	Solution	$81{\cdot}3 \times 10^{-6}$ c.g.s.	20°

Summary.

The precautions necessary for steadiness in the heterodyne beat method are described, employing frequencies greater than 10^5 per second, and it is shown that under normal laboratory conditions a beat note can be obtained perfectly steady for large periods.

Some applications of the method to physical measurements are then considered, the changes in frequency being consequent on changes in the inductance of one of the circuits. These latter changes were brought about by inserting a specimen within the coil, and were of two kinds :—

(i.) An eddy current effect, the nature of which was examined for cylindrical specimens of different materials.

(ii.) In the case of magnetic substances, a susceptibility effect. This latter variation was employed to measure the magnetic susceptibility of several salts at frequencies ranging

* Théodoridès, *loc. cit.*

from 3×10^5 per second to 4×10^5 per second, and the results obtained are in good agreement with those previously obtained by static methods.

My best thanks are due to Sir Ernest Rutherford for many suggestions connected with the problems and for his helpful criticism and encouragement during their progress.

Cavendish Laboratory, Cambridge.
May 20, 1922.

XLVI. *On the Conditions for Elastic Equilibrium under Surface Tractions in a Uniformly Eolotropic Body.* *By* R. F. Gwyther, *M.A.**

IN a paper "On an Analytical Discrimination of Elastic Stresses in an Isotropic Body,"† I have expressed the elements of mechanical stress under tractions, and also the elements of strain, in terms of quantities which resolve on transformation of orthogonal axes in the same manner as elements of stress resolve. In this paper I propose to adapt the same method to uniformly eolotropic bodies.

Briefly, we shall have under tractions,

$$\begin{aligned}
P &= -\frac{\partial^2\phi_3}{\partial y^2} - \frac{\partial^2\phi_2}{\partial z^2} + 2\frac{\partial^2\chi_1}{\partial y\,\partial z}, \\
Q &= -\frac{\partial^2\phi_3}{\partial x^2} - \frac{\partial^2\phi_1}{\partial z^2} + 2\frac{\partial^2\chi_2}{\partial x\,\partial z}, \\
R &= -\frac{\partial^2\phi_2}{\partial x^2} - \frac{\partial^2\phi_1}{\partial y^2} + 2\frac{\partial^2\chi_3}{\partial x\,\partial y}, \\
S &= \frac{\partial^2\chi_1}{\partial x^2} + \frac{\partial^2\phi_1}{\partial y\,\partial z} - \frac{\partial^2\chi_3}{\partial x\,\partial z} - \frac{\partial^2\chi_2}{\partial x\,\partial y}, \\
T &= \frac{\partial^2\chi_2}{\partial y^2} - \frac{\partial^2\chi_3}{\partial y\,\partial z} + \frac{\partial^2\phi_2}{\partial x\,\partial z} - \frac{\partial^2\chi_1}{\partial x\,\partial y}, \\
U &= \frac{\partial^2\chi_3}{\partial z^2} - \frac{\partial^2\chi_2}{\partial y\,\partial z} - \frac{\partial^2\chi_1}{\partial x\,\partial z} + \frac{\partial^2\phi_3}{\partial x\,\partial y},
\end{aligned} \quad \ldots \quad (1)$$

where $\{\phi_1, \phi_2, \phi_3, \chi_1\ \chi_2\ \chi_3\}$ resolve as elements of a stress resolve.

* Communicated by the Author.
† Phil. Mag. July 1922, p. 274.

If $\{\theta_1, \theta_2, \theta_3, \psi_1, \psi_2, \psi_3\}$ form another set of quantities, acting also as elements of stress, we may take as the components of an arbitrary displacement

$$u = \frac{\partial\theta_1}{\partial x} + \frac{\partial\psi_3}{\partial y} + \frac{\partial\psi_2}{\partial z},$$

$$v = \frac{\partial\psi_3}{\partial x} + \frac{\partial\theta_2}{\partial y} + \frac{\partial\psi_1}{\partial z},$$

$$w = \frac{\partial\psi_2}{\partial x} + \frac{\partial\psi_3}{\partial y} + \frac{\partial\theta_3}{\partial z},$$

and therefore for the elements of strain

$$e = \frac{\partial^2\theta_1}{\partial x^2} + \frac{\partial^2\psi_2}{\partial x\,\partial z} + \frac{\partial^2\psi_3}{\partial x\,\partial y},$$

$$f = \frac{\partial^2\theta_2}{\partial y^2} + \frac{\partial^2\psi_1}{\partial y\,\partial z} + \frac{\partial^2\psi_3}{\partial x\,\partial y},$$

$$g = \frac{\partial^2\theta_3}{\partial z^2} + \frac{\partial^2\psi_1}{\partial y\,\partial z} + \frac{\partial^2\psi_2}{\partial x\,\partial z},$$

$$a = \frac{\partial^2\psi_1}{\partial y^2} + \frac{\partial^2\psi_1}{\partial z^2} + \frac{\partial^2(\theta_2+\theta_3)}{\partial y\,\partial z} + \frac{\partial^2\psi_3}{\partial x\,\partial z} + \frac{\partial^2\psi_2}{\partial x\,\partial y},$$

$$b = \frac{\partial^2\psi_2}{\partial x^2} + \frac{\partial^2\psi_2}{\partial z^2} + \frac{\partial^2\psi_3}{\partial y\,\partial z} + \frac{\partial^2(\theta_3+\theta_1)}{\partial x\,\partial z} + \frac{\partial^2\psi_1}{\partial x\,\partial y},$$

$$c = \frac{\partial^2\psi_3}{\partial x^2} + \frac{\partial^2\psi_3}{\partial y^2} + \frac{\partial^2\psi_2}{\partial y\,\partial z} + \frac{\partial^2\psi_1}{\partial x\,\partial z} + \frac{\partial^2(\theta_1+\theta_2)}{\partial x\,\partial y}. \quad \ldots \quad (2)$$

Before proceeding, I will recapitulate that if the coordinate axes are rotated about their own positions through the small angles ω_x, ω_y, ω_z, and if Ω_1, Ω_2, Ω_3 (being partial differential operators) give the consequent coefficients of ω_x, ω_y, ω_z in $\{e, f, g, a, b, c\}$ or in $\{P, Q, R, S, T, U\}$, then

$$\Omega_1 = a\left(\frac{\partial}{\partial f} - \frac{\partial}{\partial g}\right) + 2(g-f)\frac{\partial}{\partial a} - c\frac{\partial}{\partial b} + b\frac{\partial}{\partial c}$$

in the case of elements of strain, and

$$\Omega_1 = 2S\left(\frac{\partial}{\partial Q} - \frac{\partial}{\partial R}\right) + (R-Q)\frac{\partial}{\partial S} - U\frac{\partial}{\partial T} + T\frac{\partial}{\partial U}$$

in the case of elements of stress.

Both $\{\phi_1, \phi_2, \phi_3, \chi_1, \chi_2, \chi_3\}$ and $\{\theta_1, \theta_2, \theta_3, \psi_1, \psi_2, \psi_3\}$ are to follow the latter type.

The relations between these two sets in elastic equilibrium must be linear.

I shall take the invariant function (2V), which gives the potential strain-function per unit of volume in the form,

$$\begin{aligned} 2V = {} & \lambda_{11}e^2 + 2\lambda_{12}ef + 2\lambda_{13}eg + 2\lambda_{14}ea + 2\lambda_{15}eb + 2\lambda_{16}ec \\ & + \lambda_{22}f^2 + 2\lambda_{23}fg + 2\lambda_{24}fa + 2\lambda_{25}fb + 2\lambda_{26}fc \\ & + \lambda_{33}g^2 + 2\lambda_{34}ga + 2\lambda_{35}gb + 2\lambda_{36}gc \\ & + \lambda_{44}a^2 + 2\lambda_{45}ab + 2\lambda_{46}ac \\ & + \lambda_{55}b^2 + 2\lambda_{56}bc \\ & + \lambda_{66}c^2. \qquad \ldots \quad (3) \end{aligned}$$

Since V is to be an invariant function, that is, since $\Omega_1 V = 0$, $\Omega_2 V = 0$, $\Omega_3 V = 0$, we deduce that, acting on the coefficients,

$$\begin{aligned} \Omega_1 = {} & 2\lambda_{14}\left(\frac{\partial}{\partial\lambda_{12}} - \frac{\partial}{\partial\lambda_{13}}\right) + (\lambda_{13}-\lambda_{12})\frac{\partial}{\partial\lambda_{14}} - \lambda_{16}\frac{\partial}{\partial\lambda_{15}} + \lambda_{15}\frac{\partial}{\partial\lambda_{16}} \\ & + 4\lambda_{24}\frac{\partial}{\partial\lambda_{22}} + 2(\lambda_{34}-\lambda_{24})\frac{\partial}{\partial\lambda_{23}} + (2\lambda_{44}-\lambda_{22}+\lambda_{23})\frac{\partial}{\partial\lambda_{24}} \\ & + (2\lambda_{45}-\lambda_{26})\frac{\partial}{\partial\lambda_{25}} + (2\lambda_{46}+\lambda_{25})\frac{\partial}{\partial\lambda_{26}} \\ & - 4\lambda_{34}\frac{\partial}{\partial\lambda_{33}} - (2\lambda_{44}-\lambda_{33}+\lambda_{23})\frac{\partial}{\partial\lambda_{34}} - (2\lambda_{45}+\lambda_{36})\frac{\partial}{\partial\lambda_{35}} \\ & - (2\lambda_{46}-\lambda_{35})\frac{\partial}{\partial\lambda_{36}} \\ & + 2(\lambda_{34}-\lambda_{24})\frac{\partial}{\partial\lambda_{44}} + (\lambda_{35}-\lambda_{25}-\lambda_{46})\frac{\partial}{\partial\lambda_{45}} \\ & + (\lambda_{36}-\lambda_{26}+\lambda_{45})\frac{\partial}{\partial\lambda_{46}} \\ & - 2\lambda_{56}\frac{\partial}{\partial\lambda_{55}} + (\lambda_{55}-\lambda_{66})\frac{\partial}{\partial\lambda_{56}} + 2\lambda_{56}\frac{\partial}{\partial\lambda_{66}} \quad \ldots \quad (4) \end{aligned}$$

From (3) we find the elastic values for P, Q, R, S, T, U by differentiation in e, f, g, a, b, c respectively. Thus

$$P = \lambda_{11}e + \lambda_{12}f + \lambda_{13}g + \lambda_{14}a + \lambda_{15}b + \lambda_{16}c, \quad \text{etc.},$$

and we may form an apparently suitable set of values for

$\phi_1, \phi_2, \phi_3, \chi_1, \chi_2, \chi_3$ in terms of $\theta_1, \theta_2, \theta_3, \psi_1, \psi_2, \psi_3$ similarly thus :—

$$\phi_1 = \lambda_{11}\theta_1 + \lambda_{12}\theta_2 + \lambda_{13}\theta_3 + 2\lambda_{14}\psi_1 + 2\lambda_{15}\psi_2 + 2\lambda_{16}\psi_3, \text{ etc.},$$

and $$\chi_1 = \lambda_{14}\theta_1 + \lambda_{24}\theta_2 + \lambda_{34}\theta_3 + 2\lambda_{44}\psi_1 + 2\lambda_{45}\psi_3 + 2\lambda_{46}\psi_3, \text{ etc.},$$

which include all of the 21 constants.

The next step would be to substitute these values in the mechanical values of the elements of stress in (1) and equate to the elastic values found as above from (3) and (2).

We should thus obtain six independent differential equations in $\theta_1, \theta_2, \theta_3, \psi_1, \psi_2, \psi_3$. But these quantities are not independent, and we are at liberty to put each of the ψ-functions equal to zero, and thus get six independent equations in three quantities, leading to conditions which I do not pursue.

Instead, I shall follow the method used in my earlier paper and be guided by the form of equations (1). Accordingly I determine the values of ϕ_1, ϕ_2, ϕ_3 by selecting the terms affected by $\partial^2/\partial y\,\partial z$ in S, by $\partial^2/\partial x\,\partial z$ in T, and by $\partial^2/\partial x\,\partial y$ in U, both in their mechanical and elastic expressions.

We thus obtain

$$\begin{aligned}
\phi_1 &= (\lambda_{24}+\lambda_{34})\psi_1 + \lambda_{44}(\theta_2+\theta_3) + \lambda_{45}\psi_3 + \lambda_{46}\psi_2,\\
\phi_2 &= (\lambda_{15}+\lambda_{35})\psi_2 + \lambda_{45}\psi_3 + \lambda_{55}(\theta_3+\theta_1) + \lambda_{56}\psi_1,\\
\phi_3 &= (\lambda_{16}+\lambda_{26})\psi_3 + \lambda_{46}\psi_2 + \lambda_{56}\psi_1 + \lambda_{66}(\theta_1+\theta_2), \quad . \quad (5)
\end{aligned}$$

thus completely connecting the two sets of functions. A first condition to be applied is that $\Omega_1\,\phi_1 = 0$, and therefore

$$\begin{aligned}
&(\lambda_{34}+\lambda_{24})(\theta_3-\theta_2) + 2(\lambda_{34}-\lambda_{24})(\theta_2+\theta_3)\\
&+ (\lambda_{33}-\lambda_{22})\psi_1 + (\lambda_{36}-\lambda_{26}+2\lambda_{45})\psi_2 + (\lambda_{35}-\lambda_{25}-2\lambda_{46})\psi_3 \equiv 0,\\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad . \quad . \quad . \quad (6)
\end{aligned}$$

with two other identities, whose consequences we can infer by symmetry.

Thus

$$\begin{aligned}
&\lambda_{11} = \lambda_{22} = \lambda_{33} = \lambda \text{ (an invariant)},\\
&\lambda_{24} = \lambda_{34} = \lambda_{15} = \lambda_{25} = \lambda_{16} = \lambda_{26} = 0,\\
&\lambda_{14} + 2\lambda_{56} = \lambda_{25} + 2\lambda_{46} = \lambda_{36} + 2\lambda_{45} = 0. \quad . \quad . \quad (7)
\end{aligned}$$

Also, as there is no term in fa or ga in $2V$, the coefficients of $\partial/\partial\lambda_{24}$ and of ∂/∂_{34} in Ω_1 are separately zero, and

$$\lambda_{23} = \lambda - 2\lambda_{44}, \quad \lambda_{13} = \lambda - 2\lambda_{55}, \quad \lambda_{12} = \lambda - 2\lambda_{66}. \quad . \quad (8)$$

We therefore find

$$2V = \lambda(e+f+g)^2 + \lambda_{44}(a^2-4fg) + \lambda_{55}(b^2-4eg) + \lambda_{66}(c^2-4ef) + 2\lambda_{56}(bc-2ae) + 2\lambda_{46}(ac-2bf) + 2\lambda_{45}(ab-2cg) \quad . \quad (9)$$

and

$$\Omega_1 = -2\lambda_{56}\left(\frac{\partial}{\partial\lambda_{55}} - \frac{\partial}{\partial\lambda_{66}}\right) + (\lambda_{55}-\lambda_{66})\frac{\partial}{\partial\lambda_{56}} - \lambda_{45}\frac{\partial}{\partial\lambda_{46}} + \lambda_{46}\frac{\partial}{\partial\lambda_{45}}.$$

I shall now write, for convenience,

$$\lambda_{44}=\nu_1,\ \lambda_{55}=\nu_2,\ \lambda_{66}=\nu_3,\ \lambda_{56}=-\nu_4,\ \lambda_{46}=-\nu_5,\ \lambda_{45}=-\nu_6$$

and

$$2V = \lambda(e+f+g)^2 + \nu_1(a^2-4fg) + \nu_2(b^2-4eg) + \nu_3(c^2-4ef) + 2\nu_4(2ae-bc) + 2\nu_5(2bf-ae) + 2\nu_6(2cg-ab), \quad . \quad (10)$$

where

$$\Omega_1 = 2\nu_4\left(\frac{\partial}{\partial\nu_2} - \frac{\partial}{\partial\nu_3}\right) + (\nu_3-\nu_2)\frac{\partial}{\partial\nu_4} - \nu_6\frac{\partial}{\partial\nu_5} + \nu_5\frac{\partial}{\partial\nu_6}.$$

The requirement that the solid should act as an elastic solid under tractions has reduced the 21 eolotropic constants in (3) to 7 constants of elastic equilibrium in (10).

Accordingly, we find from (5),

$$\begin{aligned}\phi_1 &= \nu_1(\theta_2+\theta_3) - \nu_5\psi_2 - \nu_6\psi_3,\\ \phi_2 &= \nu_2(\theta_2+\theta_1) - \nu_4\psi_1 - \nu_6\psi_3,\\ \phi_3 &= \nu_3(\theta_1+\theta_2) - \nu_4\psi_1 - \nu_5\psi_2. \quad . \quad . \quad . \quad (11)\end{aligned}$$

The value of $2\chi_1$ is deduced from $\Omega_1\phi_2=$

$$\begin{aligned}2\chi_1 &= \nu_4(2\theta_1+\theta_2+\theta_3) - (\nu_2+\nu_3)\psi_1 - \nu_6\psi_2 - \nu_5\psi_3, \text{ with}\\ 2\chi_2 &= \nu_5(\theta_1+2\theta_2+\theta_3) - \nu_6\psi_1 - (\nu_1+\nu_2)\psi_2 - \nu_4\psi_3,\\ 2\chi_3 &= \nu_6(\theta_1+\theta_2+2\theta_3) - \nu_5\psi_1 - \nu_4\psi_2 - (\nu_1+\nu_2)\psi_3. \quad (12)\end{aligned}$$

From the value of 2V given by (10), we find the elements of elastic stress, as usual, by differentiation,

$$\begin{aligned}P &= \lambda e + (\lambda-2\nu_3)f + (\lambda-2\nu_2)g + 2\nu_4 a,\\ Q &= (\lambda-2\nu_3)e + \lambda f + (\lambda-2\nu_1)g + 2\nu_5 b,\\ R &= (\lambda-2\nu_2)e + (\lambda-2\nu_1)f + \lambda g + 2\nu_6 c,\\ S &= 2\nu_4 e + \nu_1 a - \nu_6 b - \nu_5 c,\\ T &= 2\nu_5 f - \nu_6 a + \nu_2 b - \nu_4 c,\\ U &= 2\nu_6 g - \nu_5 a - \nu_4 b + \nu_3 c. \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)\end{aligned}$$

To complete the equations, we substitute for $\{e, f, g, a, b, c\}$ from (2), equate to the mechanical elements of stress given by (1), and substitute for $\{\phi_1, \phi_2, \phi_3, \chi_1, \chi_2, \chi_3\}$ to find the six equations for condition in $\{\theta_1\ \theta_2, \theta_3, \psi_1, \psi_2, \psi_3\}$. This general process will be now simplified.

In order to carry out the scheme of this paper it has been necessary that the axes should be arbitrary and the stress-elements should be written in full. But this stage having been completed we may now select a special set of axes, and also simplify the arbitrary stress-elements.

Thus, $\{e, f, g, a, b, c\}$ act on transformation of axes as $\{x^2, y^2, z^2, 2yz, 2xz, 2xy\}$ act, as do also $\{a^2-4fg, b^2-4eg, c^2-4ef, 4ae-2bc, 4bf-2ac, 4cg-2ab\}$, and since

$$\Omega_1 = 2\nu_4\left(\frac{\partial}{\partial\nu_2}-\frac{\partial}{\partial\nu_3}\right)+(\nu_3-\nu_2)\frac{\partial}{\partial\nu_4}-\nu_6\frac{\partial}{\partial\nu_5}+\nu_5\frac{\partial}{\partial\nu_6},$$

we find that

$$\nu_1x^2+\nu_2y^2+\nu_3z^2+2\nu_4yz+2\nu_5xz+2\nu_6xy=1$$

is an invariantal ellipsoid, and the principal planes of this ellipsoid are planes of elastic symmetry in the body.

I shall take these principal planes as the coordinate planes, and consequently $\nu_4=0$, $\nu_5=0$, $\nu_6=0$, while ν_1, ν_2, ν_3 now stand for the roots of the Discriminating Cubic.

The equations (11), (12), and (13), become for these axes,

$$\phi_1=\nu_1(\theta_2+\theta_3), \qquad 2\chi_1=-(\nu_2+\nu_3)\psi_1,$$
$$\phi_2=\nu_2(\theta_3+\theta_1), \qquad 2\chi_2=-(\nu_3+\nu_1)\psi_2,$$
$$\phi_3=\nu_3(\theta_1+\theta_2), \qquad 2\chi_3=-(\nu_1+\nu_2)\psi_3,$$

$$\mathrm{P}=\lambda e+(\lambda-2\nu_3)f+(\lambda-2\nu_2)g,$$
$$\mathrm{Q}=(\lambda-2\nu_3)e+\lambda f+(\lambda-2\nu_1)g,$$
$$\mathrm{R}=(\lambda-2\nu_2)e+(\lambda-2\nu_1)f+\lambda g,$$
$$\mathrm{S}=\nu_1a, \quad \mathrm{T}=\nu_2b, \quad \mathrm{U}=\nu_3c. \quad . \quad . \quad . \quad (14)$$

It will now suffice to put $\psi_1=0$, $\psi_2=0$, $\psi_3=0$, so that

$$u=\frac{\partial\theta_1}{\partial x}, \qquad v=\frac{\partial\theta_2}{\partial y}, \qquad w=\frac{\partial\theta_3}{\partial z},$$

and it follows, from above, that $\chi_1=0$, $\chi_2=0$, $\chi_3=0$ at the same time. We shall therefore remain with only three equations in θ_1, θ_2, θ_3, when these simplifications are made.

These three equations take the form

$$\lambda\left(\frac{\partial^2\theta_1}{\partial x^2}+\frac{\partial^2\theta_2}{\partial y^2}+\frac{\partial^2\theta_3}{\partial z^2}\right)=-\nu_3\frac{\partial^2(\theta_1-\theta_2)}{\partial y^2}-\nu_2\frac{\partial^2(\theta_1-\theta_3)}{\partial z^2},$$

$$=-\nu_3\frac{\partial^2(\theta_2-\theta_1)}{\partial x^2}-\nu_1\frac{\partial^2(\theta_2-\theta_3)}{\partial z^2},$$

$$=-\nu_2\frac{\partial^2(\theta_3-\theta_1)}{\partial x^2}-\nu_1\frac{\partial^2(\theta_3-\theta_2)}{\partial y^2},$$

so that . . . (15)

$$\nu_1\nabla^2(\theta_2-\theta_3)=\frac{\partial^2}{\partial x^2}\{\nu_1(\theta_2-\theta_3)+\nu_2(\theta_3-\theta_1)+\nu_3(\theta_1-\theta_2)\},$$

with two similar equations, and

$$\left(\frac{1}{\nu_1}\frac{\partial^2}{\partial x^2}+\frac{1}{\nu_2}\frac{\partial^2}{\partial y^2}+\frac{1}{\nu_3}\frac{\partial^2}{\partial z^2}\right)\{\nu_1(\theta_2-\theta_3)+\nu_2(\theta_3-\theta_1)+\nu_3(\theta_1-\theta_2)\}=0. \quad (16)$$

Hence $\nu_1(\theta_2-\theta_3)+\nu_2(\theta_3-\theta_1)+\nu_3(\theta_1-\theta_2)$ is an Ellipsoidal Harmonic, from which $\theta_1-\theta_2$, $\theta_2-\theta_3$ can be deduced.

In a previous paper, I have dealt with the simpler case for an isotropic body, when $\nu_1=\nu_2=\nu_3=n$ and $\theta_1-\theta_2$, $\theta_2-\theta_3$ are Spherical Harmonics.

The present equations apply to crystals having three orthogonal planes of elastic symmetry.

The investigation seems interesting because it passes somewhat outside the range of elastic equilibrium, even if it is ultimately confined within that range. If we regard a piece of sound material intended to serve as a test-piece we cannot consider its potential energy of strain to be precisely in the form given by (10), although by judicious working it tends to approach that form. The actual potential energy has probably a form such as that in (3), until it has been worked. The effect of "working" simplifies the form of V in a manner perhaps comparable with the algebraic discarding of constants inconsistent with elastic equilibrium. If this comparison is not unreasonable, we may venture to extend the idea, and to imagine that an excessive exertion of traction may again alter the form of the potential energy, and introduce into V terms inconsistent with elastic equilibrium and may, if continued, lead to rupture. At any rate, the theory of rupture must lie outside the range of elastic equilibrium, though not necessarily outside the elastic stress-strain relations.

XLVII. *On the Viscosity and Molecular Dimensions of Sulphur Dioxide.* *By* C. J. Smith, *B.Sc., A.R.C.S., D.I.C., Research Student, Imperial College of Science and Technology, London* *.

RECENT work on the viscous properties of compounds which are ordinarily gaseous having been successful in elucidating the molecular structure of these compounds, it was thought that it would be interesting to apply similar methods in the case of sulphur dioxide, especially as Langmuir † has already suggested a possible arrangement of the atoms which constitute this particular molecule. This paper describes the necessary viscosity measurements for sulphur dioxide. Previously the data regarding the viscosity of this gas were very scanty and did not extend over a sufficient range of temperature to determine Sutherland's constant—a factor of almost as great an importance as that of the viscosity itself in determining the mean collision area of a molecule.

Apparatus and Method of Observation.

The apparatus and method of observation which have been used for the purpose of measuring the viscosity of sulphur dioxide have recently been fully described ‡.

Method of Experiment.

The mercury pellet, which was used to drive the gas through a capillary tube which forms part of a complete circuit consisting of this tube and a fall tube in which the pellet moves between specified marks, is the same as that which was used by the author in his experiments on carbon oxysulphide §. The time of fall for air proved to be 105·53 secs. at 18·0° C. With this time of fall the corresponding time of fall for sulphur dioxide has been compared, and, with appropriate corrections, this gives the relative viscosity of air and sulphur dioxide. From this relative value the absolute viscosity has been obtained by assuming that the viscosity of air at 18°·0 C. is $1{\cdot}814\times10^{-4}$ C.G.S. units. In addition, the variation of viscosity with temperature has been derived from comparisons of the corrected times of fall at atmospheric and steam temperatures.

* Communicated by Prof. Rankine.

† Langmuir, Journ. Amer. Chem. Soc. vol. xli. p. 868 (1919).

‡ A. O. Rankine and C. J. Smith, Phil. Mag. vol. xlii. p. 601 (1921); and C. J. Smith, Proc. Phys. Soc. vol. xxxiv. p. 155, June 1922.

§ C. J. Smith, Phil. Mag. vol. xliv. p. 289 (1922).

Preparation and Purification of the Sulphur Dioxide.

The sulphur dioxide was generated by the action of dilute sulphuric acid on sodium sulphite. It was dried by being passed through several wash bottles containing concentrated sulphuric acid, and then solidified in a U-tube surrounded by liquid air. The U-tube was then cut off from the generating apparatus, and all permanent gases removed by means of a pump. The gas was made to evaporate by removing the liquid air, and samples were collected over mercury. The chief difficulty in using this gas is to dry it sufficiently well that the motion of the pellet of mercury in the fall tube shall be smooth. It is difficult because sulphur dioxide boils at $-10°$ C., and at this temperature water has a small vapour-pressure. It was finally purified and dried in the following way, before introduction into the viscometer:—The gas was solidified in a tube maintained at $-80°$ C. by means of a mixture of solid carbon dioxide and alcohol, and all permanent gases and possible traces of carbon dioxide removed by means of a Toepler pump. Sufficient alcohol was then added to the carbon dioxide mixture to raise the temperature to $-60°$ C. At this temperature water has a negligible vapour-pressure, while sulphur dioxide is liquid and has an appreciable vapour-pressure. This enabled successive small quantities of the dry gas to be pumped off and introduced into the viscometer, which was previously exhausted, until the pressure therein was atmospheric.

Experimental Results.

Table I.

Each time recorded in this table is the mean of four observations in each direction for the whole pellet, and of three when the pellet is divided into two segments. The letters in parentheses indicate the order in which observations were made.

Temp. (deg. C.).	Time of fall (secs.). Whole pellet.	Two segments.	Capillary correction, (x).	Corrected time (t).	Time at 18°·0 C.	Time at 100°·0 C.
(a) 17·72	76·16	79·67	0·0422	72·95	73·03	
(b) 17·80	76·48	80·38	0·0463	72·95	73·01	
(c) 17·85	76·82	81·00	0·0491	73·05	73·09	
(f) 17·38	76·40	80·37	0·0471	72·80	72·97	
				Mean	...73·03	
(d) 100·0	97·10	99·32	0·0219	94·97	...	94·97
(e) 99·96	97·13	99·37	0·0220	94·99	...	95·00
					Mean	...94·99

We have $t_{18}=73{\cdot}03$ sec., and $t_{100}=94{\cdot}99$ sec.

The ratio of the viscosities at 18°·0 C. and 100°·0 C. is given by the ratio of these times; thus

$$\frac{\eta_{100}}{\eta_{18}}=\frac{t_{100}}{t_{18}}=\frac{94{\cdot}99}{73{\cdot}03}=1{\cdot}301.$$

Assuming Sutherland's law to hold over the range of temperature used in these experiments, the value of Sutherland's constant is 416. The validity of Sutherland's law for this gas over the range of temperature investigated cannot be expected to be great on account of the probable large deviations from Boyle's law which this gas may exhibit, since the temperatures at which measurements have been made are not very far removed from the boiling-point of liquid sulphur dioxide. The value of C given, and subsequent deductions depending thereon, should therefore be accepted with some reserve.

Also at 18°·0 C., $\dfrac{t_{SO_2}}{t_{air}}=\dfrac{73{\cdot}03}{105{\cdot}53}=0{\cdot}6923.$

Correcting for slip in the usual way, we obtain

$$\frac{\eta_{SO_2}}{\eta_{air}}=0{\cdot}6908.$$

Assuming that the viscosity of air at 18°·0 C. is $1{\cdot}814\times10^{-4}$ C.G.S. units, the values for SO_2 are

$$\eta_{18}=1{\cdot}253\times10^{-4}\text{ C.G.S. units,}$$

$$\eta_{100}=1{\cdot}630\times10^{-4}\text{ C.G.S. units,}$$

and by extrapolation, using Sutherland's law,

$$\eta_0=1{\cdot}168\times10^{-4}\text{ C.G.S. units.}$$

According to the usual works of reference and published papers, Vogel * is the only modern worker on this subject, and he found that $\eta_0=1{\cdot}183\times10^{-4}$ C.G.S. units.

Calculation of Molecular Dimensions.

The above results enable us to calculate for sulphur dioxide that mean area which is interpreted by Professor Rankine † as the area which the molecule presents in mutual collision with others. Chapman's ‡ formula, modified in its interpretation, as indicated above, is the basis of this calculation. The

* H. Vogel, *Berlin Diss.* p. 46, 1914.

† Proc. Faraday Soc. vol. xvii. part 3 (1922).

‡ Chapman, Phil. Trans. A. vol. ccxvi. p. 347.

value obtained is $A = 0{\cdot}94 \times 10^{-15}$ cm.^{2}, which may be subject to an experimental error of 2 or 3 per cent. It is difficult to estimate the degree of precision with which this figure represents the real dimensions of the molecule. The measurements of viscosity, owing to the comparatively small temperature range over which they extend, provide no proof that, for this gas, Sutherland's law holds. Indeed, as mentioned earlier, it is improbable that the sulphur dioxide in the circumstances of the experiments was sufficiently superheated to give the true value of Sutherland's constant. It is not unlikely that the actual mean collision area differs from that calculated by an amount appreciably greater than that attributable to experimental error.

Summary of Results.

TABLE II.

Viscosity in C.G.S. units $\times 10^{-4}$.			Sutherland's constant.	Mean collision area (cm.$^2 \times 10^{-15}$).
18°·0 C.	100°·0 C.	0°·0 C.		
1·253	1·630	1·168	416	0·94

In conclusion, the author would like to record his appreciation of the continued help and advice received from Professor Rankine, and also to thank the Goverment Grant Committee of the Royal Society for a grant which enabled the research to be undertaken.

Imperial College of Science
and Technology, London, S.W.7.
10th June, 1922.

XLVIII. *On a Simple Model to Illustrate Elastic Hysteresis.* *By* S. LEES, *M.A., St. John's College, Cambridge* *.

§ 1. *Introduction.*

MUCH material has accumulated † in recent years concerning the behaviour of metals when taken through either a series of cycles of alternate compressions and tensions, or a series of periodic shear stresses. In the main, the experimental results here utilized are those of

* Communicated by the Author.

† See *e. g.* 'Dictionary of Applied Physics,' vol. i. p. 178.

Messrs. Smith & Wedgwood, 'Journal of Iron and Steel Institute,' vol. xci. p. 374. It must be admitted that in one important respect, the results of these authors appear to differ from those of other experimenters; in that, according to the cited authors, elastic hysteresis would appear only to make itself evident under certain conditions, whereas other experimenters have been of opinion that elastic hysteresis * always occurs with stress change, even with small range of stress. Without expressing any opinion on the existence or not of elastic hysteresis with small ranges of stress, the author has taken the results of Smith & Wedgwood, and attempted to construct a simple model illustrating these results. Whilst it is not contended that the model to be described is the best possible, it does to some extent satisfy a desire to reduce to simple mathematical treatment many of the well-known elastic phenomena.

It may be here noted that the model described below in § 3, and the modification of § 9, between them illustrate a whole series of well-known phenomena, such as:

(i.) Existence of elastic hysteresis loops only under certain conditions.
(ii.) Small variation of area of loop with speed of description.
(iii.) General shape of loop.
(iv.) General character of mean-stress-strain loops obtained when slow speed periodic stress is combined with rapidly alternating stress.
(v.) Existence of two points in loop at which (limits of Hooke's law) the loop commences to depart from the straight line law.
(vi.) The production of permanent set in a material and the existence of a true elastic limit beyond which elastic recovery is impossible.
(vii.) The existence of a yield point.
(viii.) The general relationship between elastic hysteresis and the three conditions referred to in (v.), (vi.), and (vii.).
(ix.) The phenomena of slip bands.
(x.) The effect of overstrain on the two points of (v.).

So far as the author knows, such a model with its illustrations as above, is original.

Before describing the model, some reasons for ruling out ordinary viscous fluid effects as the predominating cause of elastic hysteresis will be given.

* Diminishing, of course, with the range of stress.

§ 2. *Discussion of the Problem.*

In connexion with elastic hysteresis, it seems natural to invoke viscous effects analogous to those found in viscous fluids. A very obvious idea is to introduce for a material undergoing cyclical variations of stress, a stress term always depending upon the rate of change of the corresponding strain. Thus, *e.g.*, if f denote stress, s denote the corresponding strain, we may try

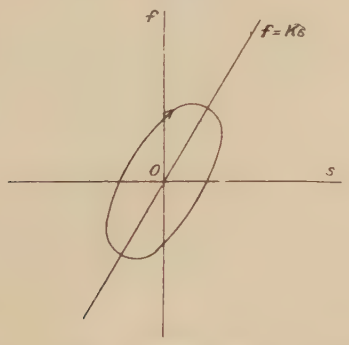
$$f = \mathrm{K}s + \lambda \dot{s}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where K and λ are constants. For the type of stress considered, K would be the ordinary modulus of elasticity. If we now make s go through a cycle given by ($t \equiv$ time)

$$s = s_0 \cos pt, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

we get different values of f which can be plotted against s, giving rise to a stress-strain loop *. This loop is clearly an

Fig. 1.



ellipse, as in fig. 1. For on eliminating t between

$$f = s_0(\mathrm{K} \cos pt - \lambda p \sin pt) \quad . \quad . \quad . \quad . \quad (3)$$

and (2), an ellipse arises. It is not difficult to verify that the area of the ellipse is proportional to both p and s_0^2. Thus with such an assumption, the area of the loop, for a given s_0, will diminish indefinitely as the speed of fluctuation

* In plotting stress-strain loops, we can always make the straight line $f = \mathrm{K}s$ have any slope we please by suitably choosing the scale for f and s; but in general this will give us a loop of minute proportions, for breadth. Having chosen a suitable slope for the above line, the loop can be magnified by representing the divergence ($f - \mathrm{K}s$), of a point of the loop from the straight line corresponding to no hysteresis, on a scale any number of times that of f. This will be assumed to have been done for the stress-strain diagrams shown in this paper.

is caused to diminish indefinitely. But this is quite contrary to the facts obtained by experiment.

The results obtained by using a formula * of the type

$$f = Ks + \lambda\dot{s} + \mu\ddot{s} + \nu\dddot{s} + \ldots., \quad . \quad . \quad . \quad (4)$$

are quite analogous. On putting $s = s_0 \cos pt$ as before, we shall get

$$f = s_0 \{\cos pt\,(K - \mu p^2 + \ldots.) - p \sin pt\,(\lambda - \nu p^2 + \ldots.)\}, \quad (5)$$

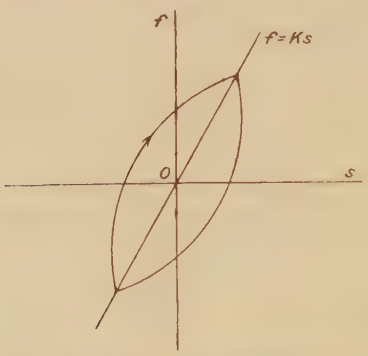
and on plotting f against s, we shall again get an ellipse. Further, whilst the area of the ellipse will not follow quite so simple a law as before, it will easily be seen that as p is made to approach zero as limit, the area (for a given s_0) will do likewise. This, again, is contrary to experience.

It may be said, in passing, that elastic hysteresis loops are not found in exact experiment to be ellipses at all. A nearer approximation to actual shapes can be found by assuming the loops to be lenticular. Such a shape can be got, *e.g.* by taking

$$f = Ks \pm \beta\dot{s}^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where the sign of the $\dot{s}^2$ term is always so to be taken as to make the frictional stress term oppose the change in strain.

Fig. 2.



Taking $s = s_0 \cos pt$ as before, it will be found that we get a diagram which is the result of eliminating t between this relation and

$$f = Ks_0 \cos pt \pm \beta s_0^2 p^2 \sin^2 pt. \quad . \quad . \quad . \quad . \quad (7)$$

If the loop be considered to be described in the clockwise sense, the plus sign will be taken from $t = -\pi/2p$ to $t = \pi/2p$. The loop is then seen to be lenticular, as in fig. 2. Here, again,

* See Maxwell, 'Collected Papers,' vol. ii. p. 623.

the area of the loop vanishes with p, and so violates the facts. A combination of formulæ (4) and (6) will suffer a like disability.

In view of the undoubted fact that when the strain range is large enough, hysteresis exists, whether the speed of describing the cycle of strain change be quick or slow, the author has felt it necessary to fall back on the rather primitive notions of solid friction. It is not contended that the ordinary ideas of fluid friction do not enter into the production of elastic hysteresis at high speeds, but it is asserted that with low speeds of describing a cyclical change, fluid friction effects are negligible.

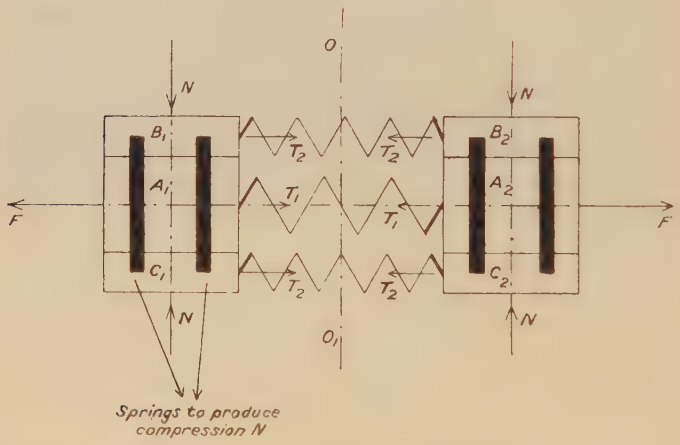
The author has found it possible, using the notions of solid friction, to get results in good qualitative agreement with many of the facts, and these notions enable mathematical analysis of a simple character to be applied. The chief factor in solid friction that is made use of in this paper is the property according to which there is a marked discontinuity between the limiting tangential force just required to produce sliding (of one surface over another pressed against it) in one direction as compared with the opposite direction. If the tangential force available lies between these limits, no slipping takes place. In fluid friction, as usually understood, the frictional force will vary continuously as the direction of relative motion or sliding is altered, and at the instant at which the two surfaces have no relative motion, the tangential force exerted by one on the other will momentarily vanish. This behaviour is totally different to that obtained with the agency of solid friction.

§ 3. *Description of a Simple Type of Model.*

In the model now to be described, the author conceives that in a metal under stress there are groups of molecules (or possibly crystals) which in some way are capable of receiving and transmitting directly a portion of the stress applied. There are also other groups of molecules which may take up a portion of the stress, but this portion is determined by considerations of solid friction. The solid friction is supposed to arise owing to the pressure of the first set of groups acting normally on the second set. This pressure may be considered as molecular in origin, and of the same character as cohesive effects. Such pressures will doubtless be large, and as a first approximation we may suppose that this pressure is not materially altered even if slipping takes place between members of the two sets of groups. It may

further tentatively be assumed that whether or not slipping takes place, the two sets of groups will behave elastically, so far as each set is concerned. These points are involved in the model shown in fig. 3. In this diagram, A_1 and A_2 represent two groups of molecules of the first kind referred to. A_1 and A_2 are directly connected up to the agency producing the stress (represented in the diagram by forces F, F), and are shown joined together elastically by a spring (marked with tension T_1 in the diagram). As typical of the groups of the second kind referred to, we have the items B_1, B_2, C_1, and C_2. Here B_1 and C_1 are between them squeezing A_1 with a pressure N. B_2 and C_2 are performing

Fig. 3.



a like office for A_2. B_1 and B_2 are shown joined together elastically by a spring (represented as being in tension T_2). C_1 and C_2 are similarly connected together by a spring (also shown in tension T_2). The diagram is intended to represent a state of affairs such that when F is zero, the tensions T_2 and the tension T_1 all vanish. Such a state of affairs may be called the *neutral* state. For such a state, the displacements of A_1, B_1, and C_1 from their equilibrium positions are all equal, and (measured with OO_1 taken as unaffected) may be denoted by x. Similar remarks apply to A_2, B_2, and C_2. Since we shall have under these circumstances

$$T_1 = \lambda_1 x_1, \quad T_2 = \lambda_2 x, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where λ_1 and λ_2 are appropriate elastic constants, it follows that

$$F = (\lambda_1 + 2\lambda_2)x. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Thus regarding F as representing externally applied stress, and x as the corresponding strain, we get the usual Hooke's law holding for stresses which do not disturb the neutral state. This remark, of course, holds for either tension or compression.

If μ denote the coefficient of solid friction between A_1 and both B_1 and C_1, the same value holding for A_2 and both B_2 and C_2, slipping will take place when

$$T_2 = \mu N. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

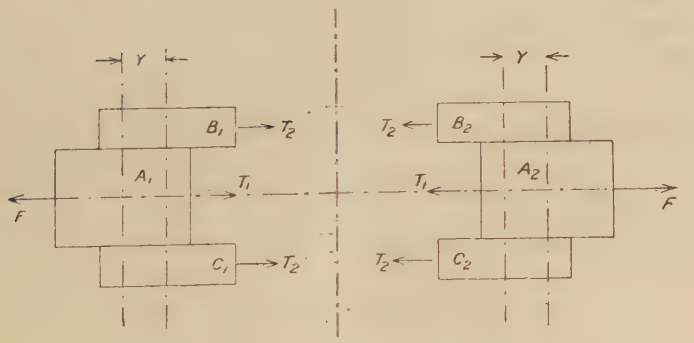
This will correspond to a value of x given by

$$T_2 = \lambda_2 x = \mu N.$$

Thus the value of F at which the linear proportional relationship between F and x breaks down will be

$$F = (\lambda_1 + 2\lambda_2)x = \frac{(\lambda_1 + 2\lambda_2)}{\lambda_2}\mu N. \quad . \quad . \quad (11)$$

Fig. 3 *a*.



If F be increased beyond this limit, slipping will take place, of amount (say) y, between A_1 and B_1 and C_1; also (see fig. 3 *a*) between A_2 and B_2 and C_2. The tensions T_2 will remain constant during such an increase of F, and we shall now have

$$F = \lambda_1 x + 2\mu N = \lambda_1 x + 2\lambda_2(x - y). \quad . \quad . \quad (12)$$

This, though a linear relationship between F and x, has a different slope from (9), and F is no longer proportional to x.

§ 4. *Elastic Hysteresis Loop for Model.*

After slipping has occurred as just explained, the moment F is caused to diminish, slipping will cease, and A_1, B_1, and C_1 (also A_2, B_2, and C_2) will move together. Thus if F_1, x_1 be the values of F and x at the instant that F is caused to decrease, we shall have at first

$$F_1 - F = (\lambda_1 + 2\lambda_2)(x_1 - x). \quad . \quad . \quad . \quad (13)$$

During any change of the type given by (13), there will be a constant amount of slip (reckoned from the neutral state) given by

$$y_1 = \frac{(\lambda_1 + 2\lambda_2)x_1 - F_1}{2\lambda_2} = x_1 - \frac{\mu N}{\lambda_2}. \quad . \quad . \quad (14)$$

It will be noticed that during the change given by (13), the slope of the F, x curve is exactly the same as that given by (9), *i. e.* as that for the neutral condition, also T_2 is now at any instant given by

$$T_2 - \mu N = \lambda_2(x - x_1), \quad . \quad . \quad . \quad . \quad (15)$$

since the slip does not alter, and $dT_2/dx = \lambda_2$.

As F goes on diminishing, ultimately becoming a force of compression, a time will arrive when slipping will once more occur. This will clearly be the case when

$$T_2 = -\mu N, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

or from (15), when

$$x = -\left(\frac{2\mu N}{\lambda_2} - x_1\right). \quad . \quad . \quad . \quad . \quad . \quad (17)$$

This corresponds to a value of F given by

$$F = \lambda_1 x - 2\mu N = -2\mu N\left(\frac{\lambda_1}{\lambda_2} + 1\right) + \lambda_1 x_1. \quad . \quad (18)$$

This result may be compared with (11). It will be noticed that the value of F given by (18) is *not* in general the negative of that given by (11). It is easy to see that further compression beyond the value given by (16) will result in a straight line law for F and x, such that

$$\frac{dF}{dx} = \lambda_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

For such further compressions, of course, sliding takes place.

If now the compression be gradually diminished, *i. e.* F be

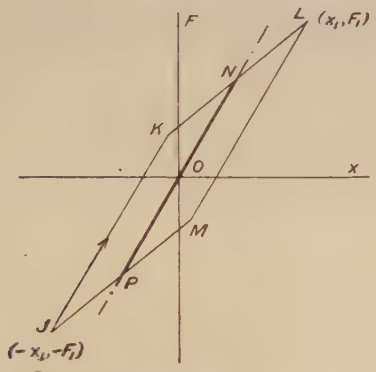
increased algebraically, we shall again go through a series of operations in which first

$$\frac{dF}{dx} = \lambda_1 + 2\lambda_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

after which (17) will hold.

By performing such reversals of stress, between limits $\pm F_1$, sufficient to cause slipping to occur in both directions, we can ultimately reach a *cyclical* condition; the stress-strain loop, *i. e.* the $F-x$ loop, being as shown in fig. 4.

Fig. 4.



The diagram is such that the limits of F are $\pm F_1$, the corresponding limits for x being $\pm x_1$.

The typical feature of the cyclic condition is, of course, that the $F-x$ loop is symmetrical with respect to the origin. In our case, the diagram is a parallelogram JKLM, with $dF/dx = \lambda_1$ for the lines KL and MJ, whilst $dF/dx = (\lambda_1 + 2\lambda_2)$ for the lines JK and LM.

To get the $F-x$ coordinates of K, the intersection of the lines JK and KL, we have for the line JK

$$F-(-F_1) = (\lambda_1 + 2\lambda_2)\,[x-(-x_1)], \quad . \quad . \quad (21)$$

whilst for the line KL we have

$$F_1 - F = \lambda_1(x_1 - x). \quad . \quad . \quad . \quad . \quad . \quad (22)$$

These two equations give for the point K :—

$$x = \frac{F_1 - (\lambda_1 + \lambda_2)x_1}{\lambda_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

$$F = \frac{(\lambda_1 + \lambda_2)F_1 - \lambda_1(\lambda_1 + 2\lambda_2)x_1}{\lambda_2}. \quad . \quad . \quad (24)$$

For the point M, the values of x and F are clearly the negatives of (23) and (24) respectively.

The value of the maximum slip (measured from the neutral state) can easily be obtained, for this must vary between (say) y_1 and $-y_1$. The range of slip is accordingly $2y_1$, and this range of slip is incurred during the description of both the lines KL and MJ. Thus $2y_1$ must equal the difference between the values of x at L and K, *i. e.*

$$2y_1 = x_1 - \frac{F_1-(\lambda_1+\lambda_2)x_1}{\lambda_2} = \frac{(\lambda_1+2\lambda_2)x_1-F_1}{\lambda_2}. \quad (25)$$

This result can also be obtained from equations (12).

Yet another expression can be obtained by remembering that at the point L, where the slip is y_1, we must have from (12)

$$\lambda_2(x_1-y_1) = \mu N.$$

Substituting the value of y given by (25), we get *

$$F_1-x_1\lambda_1 = 2\mu N. \quad . \quad . \quad . \quad . \quad . \quad (26)$$

§ 5. *Area of Hysteresis Loop.*

The area of the hysteresis loop can now be obtained. It is clearly twice the area of the triangle JKL, the coordinates (x, F) of the vertices of which are respectively $(-x_1, -F_1)$,

$$\left(\frac{F_1-\overline{\lambda_1+\lambda_2}\,.\,x_1}{\lambda_2}, \quad \frac{\overline{\lambda_1+\lambda_2}\,.\,F_1-\lambda_1\,.\,\overline{\lambda_1+2\lambda_2}\,.\,x_1}{\lambda_2}\right),$$

and (x_1, F_1). The area † is therefore

$$-\begin{vmatrix} -x_1 & , & -F_1 & , & 1 \\ \frac{F_1-(\lambda_1+\lambda_2)x_1}{\lambda_2} & , & \frac{F_1(\lambda_1+\lambda_2)-\lambda_1(\lambda_1+2\lambda_2)x_1}{\lambda_2} & , & 1 \\ x_1 & , & F_1 & , & 1 \end{vmatrix}$$

$$= \frac{2(F_1-x_1\lambda_1)}{\lambda_2}[(\lambda_1+2\lambda_2)x_1-F_1] = 8\mu N y_1, \quad . \quad (27)$$

on using (25) and (26).

This result might also have been obtained by remarking that the work lost in a complete cycle can be accounted for as due to a force of friction $2\mu N$ overcome twice (during

* When hysteresis exists, the locus of points L is therefore a straight line.

† The negative sign is used so as to make the area positive.

the stages KL and MJ) through a slip on each occasion of amount $2y_1$.

The area of the hysteresis loop clearly vanishes when $y_1 = 0$, *i. e.* when

$$F_1 = (\lambda_1 + 2\lambda_2)x_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

Using (26), we get for the corresponding limiting values of x_1 and F_1 :—

$$\left.\begin{aligned} x_1 &= \frac{\mu N}{\lambda_2}, \\ F_1 &= \frac{\mu N(\lambda_1 + 2\lambda_2)}{\lambda_2}. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (29)$$

The limiting loop for which the area just vanishes is shown in fig. 4 as the straight line PON. It is easy to verify from (23) and (24) that N is the middle point of KL, and similarly that P is the middle point of JM *.

It is to be understood that for values of x_1 and F_1 less than those given by (29), the $F-x$ relationship is always expressed by a portion of the straight line NP, whose slope is the same as that of both JK and LM, and is that corresponding to the neutral state. This statement arises from the fact that for such values of x and F, there will be no slip.

From (26) and (27) we can get two other expressions for the area of the hysteresis loop (when it exists) in the forms :

$$8\mu N\left(x_1 - \frac{\mu N}{\lambda_2}\right) = \frac{8\mu N}{\lambda_1}\left[F_1 - \frac{\mu N(2\lambda_2 + \lambda_1)}{\lambda_2}\right]. \quad . \quad (30)$$

From these we see that the area has a value proportional to the excess of x_1 over the limiting value just referred to ; alternatively, it is proportional to the excess of F_1 over its corresponding limiting value.

§ 6. *Comparison of Results obtained with Experiment.*

A large amount of data is available concerning elastic hysteresis, but, for the moment, reference will only be made to the paper by Smith & Wedgwood, *loc. cit.* figs. 2–5. The static stress-strain loops obtained by these authors for tension and compression of a material in the cyclic state agree in several particulars with the theory just outlined. Thus elastic hysteresis does not occur till the limits of stress

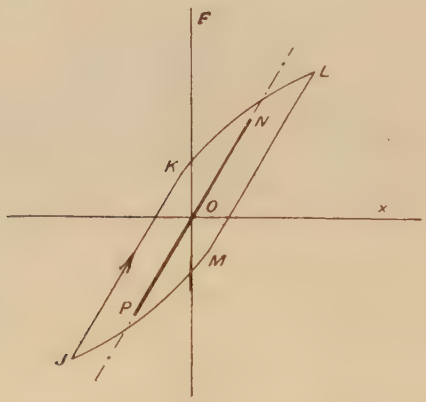
* To get the model to the neutral state from the cyclical state, we arrange for it to be put into either of the conditions corresponding to the points N or P, and then take off the load F.

exceed numerically a certain amount, and when this does occur, the area is proportional, for small-sized loops, to the excess of F_1 over the critical amount. Also, immediately after a change in sign of dF/dt, where F represents stress and t the time, the stress-strain curve is always straight and parallel to the straight line which represents elastic change without hysteresis.

On the other hand, the author's theory fails to explain two noticeable points indicated in Messrs. Smith & Wedgwood's paper:—

(1) When a point corresponding to K in fig. 4 has been reached, the stress-strain curve is actually found to become

Fig. 5.



curved, as shown in fig. 5, instead of following a straight line like KL of fig. 4.

(2) For large areas of loop, it is actually found that the proportionality between area of loop and excess of F_1 over the critical amount above referred to breaks down.

Other divergences between experiment and the theory at present outlined will be indicated below (§ 9).

§ 7. *Steady Hysteresis Loop for Unsymmetrical Stress Limits.*

We shall now discuss the nature of the steady hysteresis loop when the limits of stress are not equal and opposite. The appropriate stress-strain (in our case, $F-x$) diagram is indicated in figs. 6 and 6a. From the considerations outlined in § 4, it will readily be seen that just previous to F reaching its lowest value (as at J), the $F-x$ relation will be (on the theory outlined) $dF/dx=\lambda$. The corresponding line

in the diagram is MJ. After F has begun to increase, the $F-x$ relationship will correspond to the straight line J_1K_1, whose slope is given by $dF/dx=\lambda_1+2\lambda_2$. It will readily be seen that the steady loop ultimately described will be a parallelogram like $J_1K_1L_1M_1$ of figs. 6 or 6*a*, the slopes

Fig. 6.

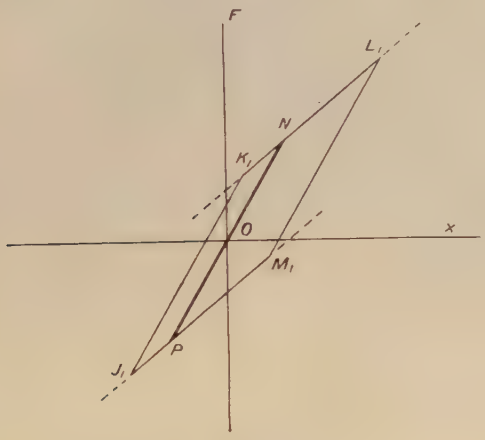
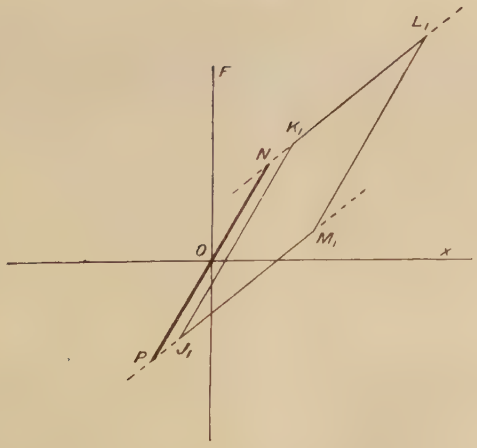


Fig. 6*a*.



of whose sides have been indicated, but the corners of which have to be found. Referring to the model shown in fig. 3, it will be understood that in describing the loop, the slip y will change in one direction and the other alternately. When slip is occurring with increase of F, the

$F-x$ relation will always be given by a portion of the line KL of fig. 4. Similarly when slip occurs with diminution of F, the $F-x$ relation is given by a portion of the line MJ. The actual loop for unsymmetrical stress limits will therefore be obtained by choosing the points L_1 and K_1 on these lines respectively, so that the stress at L_1 is F_0+F_1 and at J_1 is F_0-F_1, where $F_0 \pm F_1$ are the unsymmetrical stress limits.

It will readily be perceived from the diagram that the area of the loop will only depend on the range of variation of stress, *i. e.* on F_1; and for a given value of F_1 the diagram is got by taking $F_0=0$ (*i. e.* for the cyclic condition), and displacing it parallel to the line KL of fig. 4 until the stress limits come right.

In particular, the results of §§ 4 and 5 for the area of the loop in terms of F_1 will hold, provided we interpret F_1 as being one-half the greatest variation in stress.

We may conveniently term the state of affairs here referred to the *asymmetric cyclic state.*

For such a state we may briefly indicate the results involved.

From equation (29), provided our assumptions hold, we see that for no hysteresis to occur, F must always lie between

$$F_0 \pm \frac{\mu N(\lambda_1+2\lambda_2)}{\lambda_2}. \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where, of course, F_0 may have any fixed value.

When this condition (31) is not satisfied, the area of the loop is given by (30), where F_1 has the meaning of half the greatest variation of stress.

§ 8. *Particular Case of* $F_0=F_1$.

If the lower limit of stress for the asymmetric cyclic condition be zero, we get an interesting case. We have here to take $F_0=F_1$, and hence $F_{max.}=2F_1$. From (31) we see that the greatest value of F for no hysteresis to occur will accordingly be

$$2\mu N(\lambda_1+2\lambda_2)/\lambda_2. \quad . \quad . \quad . \quad . \quad . \quad (32)$$

This is exactly *double* the maximum stress for the cyclic condition, which just fails to produce hysteresis.

If the stress varies between O and F, and hysteresis does occur, equation (30) shows that the area of the steady loop will be given by

$$\frac{4\mu N}{\lambda_1}\left[F-\frac{2\mu N(2\lambda_2+\lambda_1)}{\lambda_2}\right]. \quad . \quad . \quad . \quad (33)$$

It is thus proportional to the excess of F over the value (32).

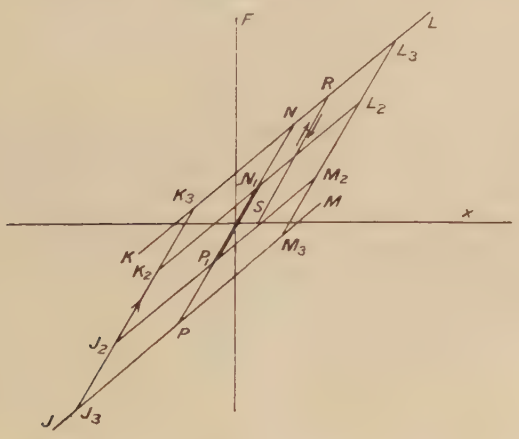
§ 9. *Effect of Rapid Periodic Changes of Stress combined with Slow Variation of Mean Stress.*

If in § 7, we imagine that F_0 changes slowly and periodically whilst the $F-x$ loop is being rapidly described under the influence of a constant F_1, we get an important case in experimental work. In such a case, we may imagine that the variation in F_0 is so slow and the periodic change of superimposed stress (between limits $\pm F_1$) so rapid, that at any instant the material is always in the asymmetric cyclic state. It is interesting to discuss the loop obtained (if any), by plotting the different values of F_0 against the corresponding *mean* values of x for the rapidly described hysteresis loops. We may call such a diagram a mean-stress-strain loop (see Smith & Wedgwood, *loc. cit.* p. 318).

There are three cases to consider :—

(*a*) If the limits of stress F_0+F_1, F_0-F_1, are such that the corresponding points in the $F-x$ diagram lie between the lines KL and MJ of fig. 4, then the mean-stress-strain

Fig. 7.



loop reduces to a straight line. This straight line will either be a portion of the line PON, or a portion of some line parallel thereto. For the neutral condition, the points P_1 and N_1 which limit this type of mean-stress-strain curve, will clearly have values of F_0 given by minus and plus respectively an amount given by subtracting the amplitude of F_1 from the value of F at N (see fig. 7).

(*b*) Using $|F_0|$ and $|F_1|$ as amplitudes or positive limiting values, we may still consider the case of $|F_1|$ less than the

value of F corresponding to the point N ; call this value F_N (given by equation (11)). Keeping $|F_1|$ constant and slowly allowing F_0 to increase from zero, we ultimately get (on the mean-stress-strain curve) to the point N_1, corresponding to the maximum stress F_N. Further increase of the maximum stress can only be obtained with slip, and such maximum stresses must correspond to points lying on the line KL. During the rapid variation of F_1, whenever the $F-x$ point on the diagram leaves the line KL, it will do so to travel along a line (like RS) parallel to PON, and must return to the line KL at the same point that it left it (since during this travel there is no slip). Hence the line of the mean-stress-strain curve corresponding to the description of the line KL will be K_2L_2, a line parallel to KL (see again fig. 7). The complete mean-stress-strain diagram for the complete cyclic variation of F_0 is therefore given by $J_2K_2L_2M_2$. It will be noticed that it is of similar type to the static stress-strain loop of fig. 4, *i. e.* its sides are parallel to the sides of the parallelogram JKLM of fig. 4.

If we draw in the static hysteresis loop $J_3K_3L_3M_3$ corresponding to the range $\pm(|F_0| + |F_1|)$, we see at once that the area of the mean-stress-strain loop $J_2K_2L_2M_2$ is $(F_N - |F_1|)/F_N$ times that of $J_3K_3L_3M_3$, and is therefore by (30) given by

$$\frac{8\mu N}{\lambda_1}\left[1-\frac{\lambda_2|F_1|}{\mu N(\lambda_1+2\lambda_2)}\right]\left[(|F_0|+|F_1|)-\frac{\mu N(\lambda_1+2\lambda_2)}{\lambda_2}\right]. \quad . \quad . \quad . \quad (34)$$

(*c*) We lastly consider the case of $|F_1|$ greater than F_N. In this case, the rapid variations in $|F_1|$ will always cause the $F-x$ or state point of the model to move from the line KL to the line MJ (or *vice versa*). A point on the mean-stress-strain curve is therefore always to be regarded as the geometrical centre (or centre of gravity) of a loop in the form of a parallelogram like J′K′L′M′ of fig. 7 *a*, such loop corresponding to some asymmetric cyclic condition. The locus of such centre of area is clearly a straight line UOV, passing through O and lying parallel to KL or JM. In such a case, therefore, the area of the mean-stress-strain loop vanishes. For a given $F_0|$ and $F_1|$, it is easily verified that the x coordinate in the diagram (fig. 7 *a*) of the end point V of this line is given by $|F_0|/\lambda_2$, the corresponding value of F being $|F_0|$.

We may compare these results for mean-stress-strain loops with those given by Smith & Wedgwood (*loc. cit.*).

The two sets of results are in many ways in agreement. Smith & Wedgwood found that, provided the amplitude of F_1 was not too great, the mean-stress-strain curve was a straight

Fig. 7 *a*.

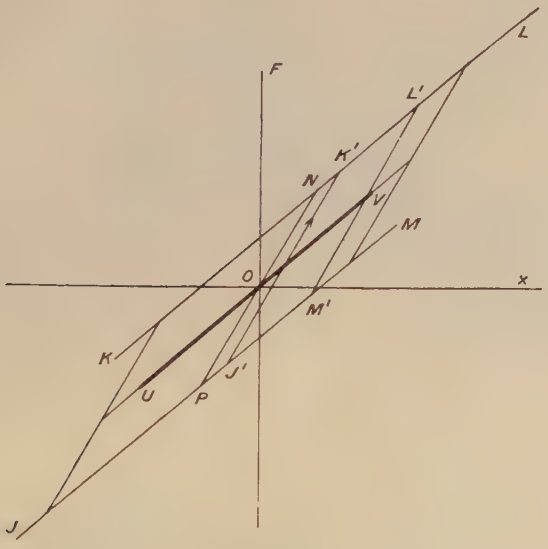
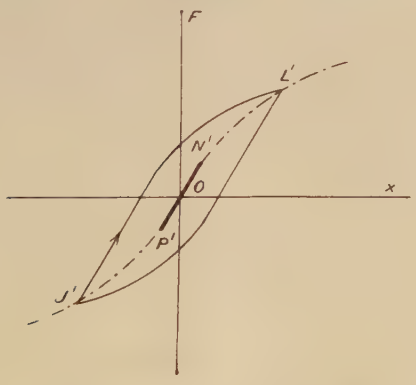


Fig. 7 *b*.



line for values of $|F_0|$ which did not exceed certain limits depending on $|F_1|$. These limits were sharply defined, and when $|F_0|$ was caused to go outside these limits, a mean-stress-strain loop was formed. A typical diagram is shown in fig. 7 *b*. Such a loop, which increased in size with

increase of $|F_0|$, was generally quite similar in character to the static stress-strain loops referred to in § 6.

The limits just referred to correspond to P_1 and N_1 of our fig. 7. If we take the static elastic limits for zero hysteresis loops given by Smith & Wedgwood's fig. 14 as 9·5 tons per in.^{2}, and consider the case indicated in the same authors' fig. 15, viz. $|F_1 = 7{\cdot}65$, we ought by (*a*) of this section to get for the point N_1 of our fig. 7 a value of

$$F = 9{\cdot}5 - 7{\cdot}65 = 1{\cdot}85 \text{ tons per in.}^2.$$

The actual value indicated in Smith & Wedgwood's fig. 15 would appear to be about 1·6 tons per in.^{2}.

A difficulty arises in connexion with the differences in the stress limits for zero hysteresis loops as shown in Smith & Wedgwood's figs. 2 and 14. The two results of these figures can be to some extent reconciled by assuming that repeated slip causes some change in the value of μ in the model, *e.g.* by temperature change, etc. Ultimately, of course, the explanation is molecular, but the fact that rest causes the material to go from a state corresponding to Smith & Wedgwood's fig. 2 to a state corresponding to their fig. 14. is a good reason for taking this simple explanation.

There are certain outstanding differences between the results obtained from the model of § 3, and the actual results of Smith & Wedgwood. The first is that the mean-stress-strain loop is not a parallelogram in actual experiment. This has been already noted. Further, when the loop does not reduce to a straight line, it is found experimentally that for a given $|F_1|$, variation of $|F_0|$ causes the points of maximum F_0 (corresponding also to points of maximum strain) to lie on a curve like N′L′ of fig. 7 *b*. According to the present theory, this curve should be a straight line (parallel to KL of fig. 4).

In an attempt to meet the objections just raised to the model of § 3, and those mentioned at the end of § 6, the author now puts forward a slightly modified theory and model.

§ 10. *Modified Model.*

Fig. 8 shows a modification of the model described in § 3. It will be noticed that the contacts for A_1 with C_1 and B_1 are point (or line) contacts; similarly for A_2 with C_2 and B_2. The rubbing surfaces of A_1 and A_2 are now taken as curved, instead of straight (or plane).

Fig. 8 shows the model in a configuration corresponding to the neutral condition, whilst fig. 9 shows a state of

Fig. 8.

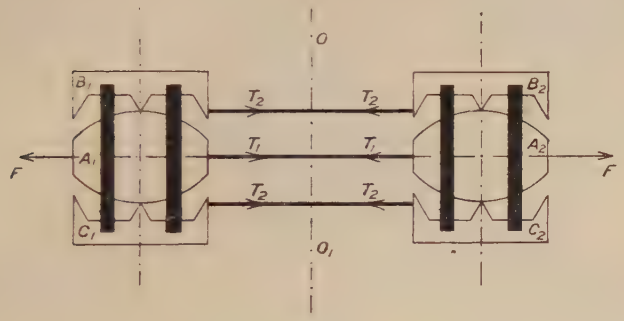


Fig. 9.

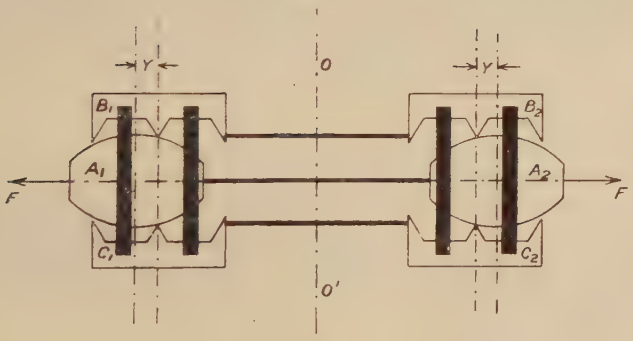
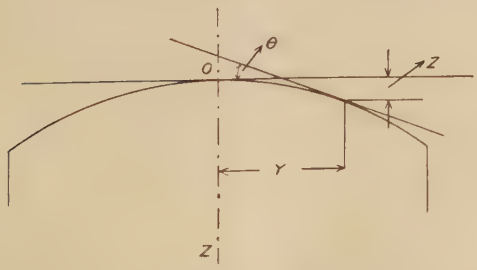


Fig. 10.



affairs when slip y has taken place. Fig. 10 gives an enlarged view of one of the two rubbing surfaces of A_1. It will be seen that the rubbing surface is taken as symmetrical about an axis Oz perpendicular to the direction of

application of the force F, the origin O corresponding to the point (or line) of contact for the neutral condition. Any equation for the surface (assuming Oy to be the tangent at O) must give z as an even function of y. To simplify the algebra, we shall assume that

$$z = ay^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

where a is constant and small. Thus for such displacements as we have to consider, the slope of the rubbing surface for any given y is given by

$$\tan\theta = \frac{dz}{dy} = 2ay, \quad . \quad . \quad . \quad . \quad . \quad (36)$$

which is also small.

Referring back to fig. 8, it will be noticed that the tensions (or compressions) T_2 are drawn so as to pass through the corresponding points of rubbing. This is done so as to avoid the consideration of tilting effects of the tensions or compressions T_2 on the pieces B_1, B_2, C_1, C_2. If such tilting effects are taken into account, it is easy to see that even with no slipping taking place, the $F-x$ relationship will not be exactly linear, but F will involve small terms in x^2 and higher powers of x.

Although the magnitudes of z to be considered are small, it is conceivable that they will exert appreciable influence on the pressure N between (say) A_1 and B_1, normal to the direction of F. We shall accordingly assume a linear relationship between N and z, and take

$$\left.\begin{aligned} N = N_0 - \alpha z = N_0 - \beta y^2, \\ \text{where } \alpha \text{ and } \beta \text{ are constants, and } \beta = 2\alpha a. \end{aligned}\right\} \quad . \quad . \quad . \quad (37)$$

For the general case of slip, the value of T_2 will be given by

$$\pm T_2 = N \tan(\phi \mp \theta), \text{ with } \mu = \tan\phi.$$

If we make the further assumption that μ is so small* that $\mu\tan\theta$ is negligible compared with unity, we get the following expressions for T_2 :—

$$\frac{dy}{dt} \text{ and } T_2 \text{ positive}, \qquad T_2 = (N_0 - \beta y^2)(\mu - 2ay), \quad . \quad (38)$$

$$\frac{dy}{dt} \text{ and } T_2 \text{ negative}, \qquad T_2 = -(N_0 - \beta y^2)(\mu + 2ay). \quad (39)$$

* This is justifiable if the cohesive forces in metals have the large values usually attributed to them as compared with the stresses here dealt with.

Starting with the model in the condition corresponding to the neutral state, and applying a gradually increasing force F, we have at first

$$F = (\lambda_1 + 2\lambda_2)x, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

exactly as in § 3. Slip movement will take place when

$$\lambda_2 x = \mu N_0 = T_2. \quad . \quad . \quad . \quad . \quad . \quad (40)$$

After this, we shall have for further increased values of F :

$$T_2 = \lambda_2(x-y) = (N_0 - \beta y^2)(\mu - 2\alpha y). \quad . \quad . \quad (41)$$

The relation between y and x is therefore the cubic equation

$$y^3 - \frac{\mu}{2\alpha} y^2 + \frac{(\lambda_2 - 2\alpha N_0)}{2\alpha\beta} y - \frac{(\lambda_2 x - \mu N_0)}{2\alpha\beta} = 0. \quad . \quad (42)$$

If we consider such displacements that $(N_0 - \beta y^2)$ is always positive, it is physically obvious that there must be a real positive root of y for any given value of x (which value must of course be such that $\lambda_2 x > N_0\mu$). The real positive value of y can also be shown to exist by putting successively $y=0$ and $y=\infty$ in the left-hand side of (42), when there appears a change of sign.

As y goes on increasing, a time will come when T_2 will vanish. This, from (41), will clearly be the case when

$$y = \mu/2\alpha, \quad \text{and} \quad F = \lambda_1\mu/2\alpha. \quad . \quad . \quad . \quad (43)$$

Further increase of y will result in T_2 becoming negative, *i. e.* becoming a compression. If after this has occurred, F is caused to diminish, ultimately becoming a compression, it is easily seen that T_2 will always remain negative, as friction and slope θ will now be assisting each other. No matter what compression may correspond to T_2, y cannot be caused to diminish. Thus the value of y given in (43) really corresponds to the beginning of *permanent set*. For values of F beyond that given by (43), complete recovery cannot be afterwards attained. We may therefore call this value of F the *elastic limit*. It is to be distinguished from the value of F obtained from (9) and (40), viz.

$$F = \frac{(\lambda_1 + 2\lambda_2)\mu N_0}{\lambda_2}. \quad . \quad . \quad . \quad . \quad . \quad (44)$$

This latter limit corresponds to the *limit of Hooke's law*. For values of F less than this, Hooke's law will be accurately followed, and there will not be any hysteresis effects.

If F be increased continually beyond the value given by

(43), not only will T_2 become negative, but dT_2/dx will become negative and numerically increase with x or y. This may be seen at once physically, or may be verified by the algebra of (41) and (42). Thus a time will in general arrive when $dT_2/dx = -\frac{1}{2}\lambda_1$, and when this is the case,

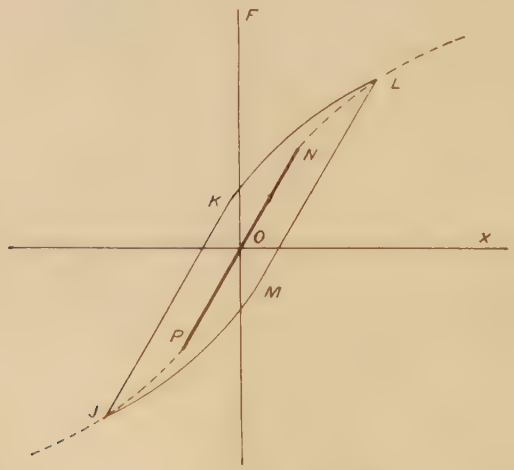
$$\frac{dF}{dx} = \lambda_1 + \frac{2dT_2}{dx} = 0.$$

This would correspond to *yield point*, as ordinarily understood in the testing of materials.

With regard to the term $(N_0 - \beta y^2)$ which has been frequently utilized in this section, we can suggest a rough interpretation. It is essentially to be regarded as a force of cohesion. Hence the value $y = \sqrt{N_0/\beta}$ must be regarded as a slip sufficient to break down this cohesion. Thus it may roughly be identified with the slip producing *fracture or failure*. In this connexion, it should be borne in mind that the model is only a rough representation of what is essentially a statistical problem, involving a multiplicity of surfaces, whose normals and corresponding cohesive forces act in all directions.

§ 11. *Cyclic State for Modified Model.*

Fig. 11.



We proceed to discuss the nature of the hysteresis loop for the model when in the cyclic condition. The appropriate diagram is shown in fig. 11. The points L and J refer to

the states (F_1, x), $(-F_1, -x_1)$ respectively; whilst the corresponding slips are y_1 and $-y_1$ respectively. We shall suppose that y_1 is less than $\mu/2a$, so that the cyclic condition is possible. By (42), we shall have

$$y_1^3 - \frac{\mu}{2a}y_1^2 + \frac{(\lambda_2 - 2aN_0)}{2a\beta}y_1 - \frac{(\lambda_2 x_1 - \mu N_0)}{2a\beta} = 0. \quad (45)$$

F_1 is then given by

$$F_1 = \lambda_1 x_1 + 2\lambda_2(x_1 - y_1) = (\lambda_1 + 2\lambda_2)x_1 - 2\lambda_2 y_1. \quad (46)$$

Now imagine F diminished, corresponding to the path LM. At first, we shall have

$$\frac{dF}{dx} = (\lambda_1 + 2\lambda_2), \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and this will go on till slip occurs at M. If the value of x at M be x_M, the value of T_2 there will be

$$(T_2)_M = (N_0 - \beta y_1^2)(\mu - 2ay_1) - \lambda_2(x_1 - x_M), \quad . \quad (47)$$

which must be a compression sufficient to cause slip. Hence also

$$-(T_2)_M = (N_0 - \beta y_1^2)(\mu + 2ay_1). \quad . \quad . \quad . \quad (48)$$

From (47) and (48) we get

$$\lambda_2(x_1 - x_M) = \mu(N_0 - \beta y_1^2). \quad . \quad . \quad . \quad (49)$$

For a given x_1, (45) determines y_1, and then (46) gives F_1. From (49) we can find x_M, and the appropriate value of F at M is easily obtained, since the point L and the slope of LM are both known. The points J and K are got by symmetry from L and M respectively.

To get the shape of the curve KL (and therefore by symmetry JM), let at any point of the curve the slip be y. Then (42) holds and gives y in terms of x, say $y = f_1(x)$. Also

$$F = \lambda_1 x + 2T_2 = \lambda_1 x + 2(N_0 - \beta y^2)(\mu - 2ay); \quad . \quad (50)$$

hence on eliminating x between $f_1(x)$ and F, we get the required $F - x$ relation for the curve KL. Without going into the algebra, it is quite clear physically that the shape must be something like that shown.

The area of the complete loop is most easily obtained by observing that energy is lost on the whole, only during the

process of slip. Along KL the loss by friction is therefore

$$2\int_{-y_1}^{y_1} T_2 dy = 2\int_{-y_1}^{y_1} (N_0-\beta y^2)(\mu-2ay)dy, \quad . \quad (51)$$

whilst along the path MJ, the loss is

$$2\int_{y_1}^{-y_1} T_2 dy = -2\int_{y_1}^{-y_1} (N_0-\beta y^2)(\mu+2ay)dy. \quad (52)$$

By changing y into (say) $-u$ in (52), we see that (51) and (52) give the same result, as might be expected. Hence the total loss by friction in describing the loop is

$$4\int_{-y_1}^{y_1} (N_0-\beta y^2)(\mu-2ay)dy = 8\mu y_1\left(N_0-\frac{\beta}{3}y_1^2\right). \quad (53)$$

This is the required area of the loop. It clearly vanishes when the slip y_1 vanishes.

When the slip y_1 is small, a first approximation for y_1 is from (45),

$$y_1 = (\lambda_2 x_1-\mu N_0)\,/\,(\lambda_2-2aN_0). \quad . \quad . \quad . \quad (54)$$

A nearer approximation is therefore

$$y_1 = \frac{\lambda_2 x_1-\mu N_0}{\lambda_2-2aN_0} + \mu\beta\frac{(\lambda_2 x_1-\mu N_0)^2}{(\lambda_2-2aN_0)^3}. \quad . \quad . \quad (55)$$

Hence from (53) and (55), as x_1 and y_1 increase, the area of the loop increases at a greater rate than $(\lambda_2 x_1-\mu N_0)$. This result may be compared with the results of § 5, and the comments in § 6.

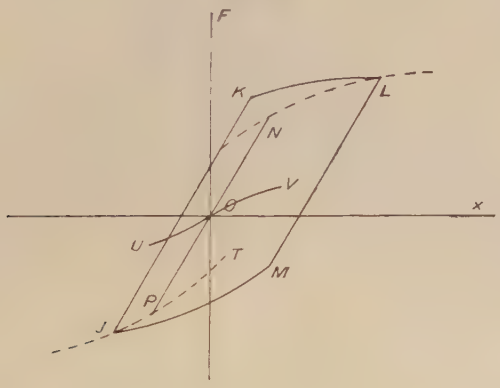
§ 12. *Asymmetric Cyclic condition for Modified Model.*

We can work out the case of a hysteresis loop produced with unsymmetrical stress limits, following the procedure of § 7. A typical resulting loop is shown in fig. 12, which shows a case with the mean stress F_0 positive. The point L will still lie on the dotted curve NL of fig. 11, whilst the point J will also lie on the dotted curve JP of the same figure. The new curves KL and MJ will not, however, be symmetrical about the origin O. As F_0 is increased, the point J will ultimately coincide with P, and further increase of F will result in J lying on the curve PT, which is the continuation to the right of P, of the curve JP. A limiting case of elastic hysteresis will arise when F_0 is increased to such an extent that JK just touches the curve JPT. This

will, of course, correspond to an amount of slip given by equation (43). Further increase of F_0 will clearly involve permanent set.

In the above argument, it is supposed that the variations of F_0 have been made with the range $2|F_1|$ of the alternating stress kept constant.

Fig. 12.



The expression for a typical area of loop in the general case is complicated, and is not given here.

For small slips y, it is clear that the results of calculation for our original model can be used.

§ 13. *Mean-stress-strain Loop for Modified Model.*

Following the argument of § 9, we can consider for the modified model the effects of superposing a periodic slow variation of mean stress on a rapidly alternating stress.

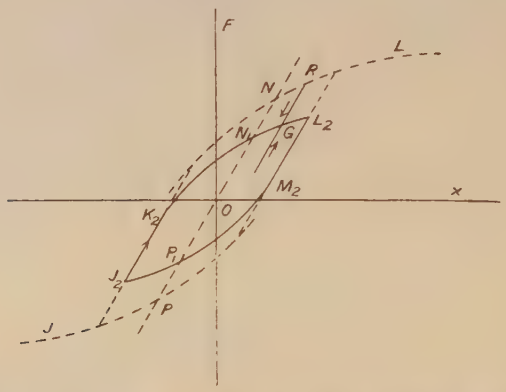
There are three cases to consider —

(*a*) Starting from the neutral condition, provided $|F_0|$ and $|F_1|$ are small enough, the mean-stress-strain curve will be a portion of the straight line PON of fig. 11. The limiting points of this line will be given exactly as in (*a*) of § 9.

(*b*) With $|F_1|$ less than F_N, but $|F_0| + |F_1| > F_N$, we shall get hysteresis loops of the mean-stress-strain type arising. Referring to fig. 13, a typical loop like $J_2K_2L_2M_2$ will consist of lines J_2K_2 and L_2M_2 parallel to the straight line PON, and two curves $K_2N_1L_2$ and $M_2P_1J_2$. The curve $K_2N_1L_2$ is clearly obtained as the locus of points G such that GR drawn upwards and parallel to PON from G to R (a point on the curve NL) is exactly equal to $|F_1|$. The

curve $M_2P_1J_2$, which is symmetrical with $K_2N_1L_2$ about the origin, is similarly obtained from the curve PJ (compare with fig. 7 *b*) *.

Fig. 13.



(*c*) With $|F_1| > F_N$, we get hysteresis loops whatever be the value of $|F_0|$. The mean-stress-strain-curve, *i. e.* the locus of the point given by the mean of the extreme stresses and the mean of the extreme strains for an instantaneous loop with the given $|F_1|$ corresponding to any values of F_0, is therefore a curve like UOV, of limited length (see fig. 12). Provided permanent set does not take place, the length of UOV will be determined by *both* of the values of $|F_0|$ and $|F_1|$, and not merely by $|F_0|$, as in § 9 (*c*). A limitation is set up to the value of $|F_0| + |F_1|$ by the restriction that no permanent set shall take place. The algebraic details are not given here.

§ 14. *Application of Model to Shear Stresses.*

The model of § 3 and its modification of § 10 can also be used to illustrate elastic hysteresis for shear stresses. Referring, *e. g.* to fig. 3, we have only to imagine the force F now applied to B_1 instead of A_1, and the equal and opposite force applied to C_2 instead of A_2, to get a model showing shearing action. We are here neglecting the consequent tilting of the portions of the model; this tilting may be avoided by supposing the component parts to be constrained to move parallel to the forces F by suitable frictionless guides. Whilst it is not intended that any comparison

* Notice, however, that our theory would make the dotted line N′L′ of fig. 7 *b* always coincide with a curve of the mean-stress-strain diagram, which apparently is not the case.

between the cases of direct and shear stresses shall be made numerically, it is quite clear that such a model will lead to exactly the same *type* of results in the two cases. A comparison of the preceding theory with the results of Mr. F. E. Rowett's experiments is satisfactory in many ways. These experiments dealt solely with shear stress hysteresis (see Proc. Roy. Soc. A. vol. lxxxix. p. 528 *et seq.*).

§ 15. *Time Effects.*

It is quite clear that the model and its accompanying theory do not explain what may be called *time effects* in elastic solids. By this phrase is meant here the changes which take place in a solid with lapse of time, with or without the application of external stress (kept constant). Some account can be rendered of these effects by assuming that when slip takes place, the frictional force of slipping is not a constant as in the model of § 3, or a function of the slip as in the modification of § 10, but depends also on the *velocity of slip*, not on the rate of change of the strain. The difficulties arising out of time effects have been avoided in the above discussions as far as possible. They are regarded as arising out of change of μ with velocity. This "coefficient of friction" will doubtless depend not only on the velocity of rubbing, but also on temperature, which in turn is a function of the number of hysteresis cycles described, etc. In this connexion, it should be observed that the introduction of μ into the argument of the paper is essentially an artifice which brings out the striking analogy which seems to hold between the every-day phenomena of solid friction, and the more subtle friction obtained in elastic hysteresis experiments.

Conclusion.

In this paper the author has described a simple model which would seem in many ways to bring out, at least qualitatively, many of the general effects observed in connexion with elastic hysteresis. The ultimate standpoint is that such effects are due to something analogous to the ordinary solid friction of every-day life. The model enables some simple deductions to be drawn of a mathematical character, but no attempt is made here to stress these deductions unduly, as the model (involving one dimension of displacement) can only but roughly represent what is essentially a question of statistics, involving slippings in all conceivable directions.

XLIX. *Atomic Hydrogen and the Balmer Series Spectrum.*

By R. W. Wood, *Professor of Experimental Physics, Johns Hopkins University* *.

Part I. *Atomic Hydrogen.*

IN the present paper an explanation will be given of practically all of the very curious spectroscopic phenomena observed with very long vacuum tubes containing hydrogen, which I described in two previous communications (Proc. Roy. Soc. vol. xcvii. ; Phil. Mag. vol. xlii. p. 729).

The explanation has apparently been found of the necessity for water vapour or oxygen for the development of the Balmer spectrum—a matter which has always been a mystery. Very remarkable effects have been obtained, which show how important is the rôle played by the wall of the tube and the gas film adsorbed on it. It has been found possible to pump practically pure atomic hydrogen gas out of the discharge tube and study its chemical and physical properties. Wires of certain metals and certain oxides, when introduced into the stream of atomic hydrogen, come spontaneously to incandescence and cause the formation of molecular hydrogen.

To make the present paper intelligible, it will be necessary to recapitulate very briefly the subjects taken up in the two earlier communications.

It was found that if a hydrogen vacuum tube of moderate bore (4 to 6 mm.), and a metre or two in length, was excited by the discharge of a high-potential transformer (or the direct current from a battery of dynamos), the central portion of the tube showed only the lines of the Balmer series, the secondary spectrum appearing only in the vicinity of the electrode bulbs at the ends of the tube. By using the central portion (suitably bent) "end-on," the series was photographed to the 20th line—a gain of eight lines over previous laboratory records.

The hydrogen was introduced moist from an electrolytic generator through a long fine capillary, and continuously withdrawn from the tube by a mercury pump.

With small currents (0·5 to 1·5 amps.) in the primary of the transformer, the luminosity of the tube was low, and the secondary spectrum predominated, the Balmer lines being very weak. As the current was increased, the Balmer lines increased, and the secondary spectrum *decreased* in intensity, reaching its minimum value with a

* Communicated by the Author.

current of 15 or 20 amperes in the transformer. The actual intensity of the secondary spectrum (at its minimum) was about 1/50 of the intensity which it had at the ends of the tube.

As we shall see later on, the probable explanation of the peculiarities thus far outlined is as follows:—The secondary spectrum is emitted by the hydrogen molecules; the Balmer lines by the atoms.

With a heavy current in the tube, the dissociation into atoms is nearly complete and permanent, no appreciable recombination occurring during the very brief current-pauses which occur when the transformer potentials are near the zero value, the duration of which can be observed by viewing the discharge in a revolving or "wabbled" mirror. This time is of the order of 1/1500 sec., and, as we shall see presently, about 1/5 of a second is required for the recombination of the atomic hydrogen.

At the ends of the tube, molecular hydrogen is continuously supplied by the bulbs, the metallic electrodes acting as catalyzers causing the instantaneous recombination of the dissociated hydrogen. The probability of the truth of this explanation will appear when we come to the subject of the action of metallic wires on the discharge.

With a feeble current, however, atomic hydrogen is not formed rapidly enough to permit of high concentrations, and the secondary spectrum predominates in consequence. With the heavy current, about 1/50 sec. is required for the dissociation of all of the molecular hydrogen in the central portion of the tube. This we know from the study of the duration of what I called the "secondary spectrum flash."

It was found that with the tube operating under such conditions a direct-vision prism showed only the Balmer lines in the central portion, the intervening regions being quite black (the "black stage"); if the current was interrupted for a moment and then turned on again, the secondary spectrum appeared as a brilliant flash, which lasted from one to three or four half-cycles of the current, according to the pressure of the gas in the tube. At high pressures the duration of the flash was longer, as was to be expected, more time being required for the complete breakdown of the gas into atoms.

The further extension of the Balmer spectrum depends upon ascertaining the cause of, and abolishing, the secondary spectrum and the faint continuous background, and giving a sufficiently long exposure. The most promising line of

attack appeared to be a study of the "Infected spots" which I spoke of in the earlier papers. These are portions of the tube in which the discharge appears white or pink, in contrast to the fiery purple exhibited by the remainder of the tube. The spectrum of these spots shows the Balmer series only to the 12th or 14th member, and a fairly strong secondary spectrum. I suspected that they were due to a contamination of the wall of the tube; and if the cause could be found, it might be possible to improve in some way the condition of the rest of the tube, and so obtain a more complete series of Balmer lines.

The clue was obtained, as I have shown in a recent paper in the Proc. Roy. Soc., by the accidental entrance of a speck of sealing-wax into the discharge tube. This was speedily changed to a spot of stannous oxide by the heat of the discharge, and examination of the spot with a lens showed that it was covered with minute globules of metallic tin.

A section of tube was now fine-ground on the inside with carborundum, and this ground portion made a part of the long hydrogen tube; the portions to the right and left of the ground portion were purple, and showed the pure Balmer spectrum, while in the ground portion the discharge was white, and showed a very strong secondary spectrum.

The ground-glass tube was tried as a result of an experiment with a tube of unglazed porcelain, inserted at the middle of the tube, which was then bent at two right-angles, so that the discharge in the porcelain tube could be viewed or photographed "end-on." The porcelain tube gave only secondary spectrum with the first four or five Balmer lines.

A tungsten wire was then inserted in the tube at a spot which showed the pure Balmer spectrum. The wire was raised to a white heat by the discharge, though a fine thread of soft glass inserted in the same way was not even softened. In the vicinity of the wire the secondary spectrum came out strong, and further experimenting showed that the secondary spectrum appeared a second or so before the wire became incandescent. Addition of oxygen to the hydrogen suppressed the heating of the wire.

As I have shown in the paper previously alluded to, the action of the wall of the tube at an infected spot, the speck of stannous oxide, the tungsten wire, and the ground-glass surface appears to be a catalytic one, these surfaces causing a recombination of the atomic hydrogen, thus furnishing molecular hydrogen at a rapid rate, the breakdown of which by the current causing the secondary spectrum.

In all of the recent work, tubes of pyrex glass, carefully cleaned with hot chromic acid, have been used. The tubes usually get into good condition after a few minutes' operation, and show less luminosity through a green ray-filter (which is opaque to the Balmer lines) than the tubes of soft glass used in the earlier work.

One of the most discussed problems in spectroscopy is why the presence of water vapour in the hydrogen enhances the Balmer series and suppresses to a great degree the secondary spectrum. As I showed in the earlier papers, if dry hydrogen is employed in the long tube, fed in at intervals through a palladium tube and pumped out with the tube in operation, the discharge eventually becomes white, and all of the Balmer lines disappear except H_α, which is so faint that it appears of a dull brick-red colour, in contrast with the secondary spectrum. In view of what we now know, it appears as if the glass wall of the tube, when thoroughly freed from adsorbed water vapour or oxygen, acts as a powerful catalyzer of the atomic hydrogen, which never reaches a sufficient concentration to cause the Balmer spectrum to appear.

Dr. Irving Langmuir, with whom I discussed these results, made the very valuable suggestion that the glass surface might be "poisoned" by the oxygen. He has found, in the course of an extended study of the production of atomic hydrogen by an incandescent tungsten wire, that the presence of small traces of oxygen prevented the formation of atomic hydrogen by "poisoning" the catalyzing surface of the metal. This being the case, the oxygen must also render the surface of the (comparatively) cold tungsten incapable of bringing about the recombination of the atomic hydrogen, as had been found to be the case.

This makes it appear extremely probable that the part played by water vapour in bringing out the Balmer series is merely that of supplying a "poison" (oxygen) for the catalyzing wall of tube, thus permitting a high concentration of atomic hydrogen in the tube under the action of the heavy discharge. With a feeble discharge, as I showed in the earlier paper, the secondary spectrum predominates and the Balmer lines are weak. This is probably due to the fact that the atomic hydrogen is not formed fast enough to get ahead of the catalyzing power of the tube wall.

If dry hydrogen is admitted through palladium, and the tube brought to the white stage by long operation, it is found that if a condenser is put in parallel with the tube, the discharge becomes red and the Balmer lines appear.

The action of a condenser is to pass currents of enormous magnitude but of very brief duration through the tube.

With these very heavy currents (hundreds or even thousands of amperes) we have a sufficient momentary concentration of atomic hydrogen to bring out its characteristic lines, even with the tube wall thoroughly freed from water vapour—the condition which gives the secondary spectrum only, owing to the powerful catalyzing action of the walls.

Merton's observation that the discharge became white when the hydrogen tube was immersed in liquid air, is at once explained by the greater catalyzing power possessed by the wall at a low temperature. Langmuir found that the atomic hydrogen produced by incandescent tungsten would not pass through a tube cooled by liquid air, though it passed to a considerable distance down a tube at room temperature. This observation I have confirmed in the study of the properties of atomic hydrogen, pumped from a discharge tube operated by a heavy current, small particles of thorium oxide being brought to incandescence at a distance of 20 cm. from the discharge tube. Touching the wall of the tube leading to the pump with a pad of cotton wet with liquid air, at once extinguished the specks of thoria in the tube beyond the cooled spot. A fine tungsten wire, inserted in the tube leading to the pump at a distance of 4 or 5 cm. from the discharge tube, is brought to a red heat by the current of atomic hydrogen pumped from the tube. Clean aluminium foil of the thickness of writing-paper, when introduced into the discharge tube, at first caused the appearance of the secondary spectrum in its vicinity, but after several minutes' operation the deep purple colour returned and the secondary spectrum disappeared. If the hydrogen current was now shut off and air admitted, and the tube operated with air at about 0·5 mm. for a few minutes, it was found that, on again operating it with hydrogen, the aluminium had regained its catalyzing power, and the white discharge appeared in its vicinity; in a few minutes this disappeared, however, as before. This makes it seem probable that slightly oxidized aluminium will catalyze the atomic hydrogen, but that the clean metal will not.

The mystery of why the long tube gives a pure Balmer spectrum at the centre now appears to be explained. The more or less oxidized aluminium electrodes act as catalyzers supplying molecular hydrogen continuously from the atomic hydrogen formed by the discharge, and the concentration of the atomic gas never reaches a high value at the ends of the

tube near the electrode bulbs. In one tube of pyrex glass which had been very carefully cleaned with chromic acid, with especially clean bright electrodes, it was found that the white discharge extended to a distance of only 3 or 4 cm. from the bulbs, while in the earlier tubes it often reached to a distance of 20 or 30 cm.

In the earlier papers I have drawn attention to the circumstance that if the hydrogen tube is brought to the white stage, and then highly exhausted, with the current shut off, if a small amount of air or nitrogen is admitted, the discharge is of a most beautiful golden-yellow colour, resembling the discharge in pure helium. Photographs of the spectrum showed that the second positive spectrum (violet and ultra-violet bands) was nearly absent, the yellow colour being due to the first positive spectrum, consisting of red, yellow, and green bands.

Applying the catalysis theory to this result, the indications are that the first positive spectrum is due to the nitrogen molecule, the second to the atom. It was found that the yellow discharge was obtained only if a very small amount of air was admitted, doubtless due to the fact that if too much air was introduced there was enough oxygen to poison the walls of the tube. I have not yet been able to get the second positive spectrum free from the first, but no very great amount of work has been done in this direction. Possibly by introducing an excess of oxygen it can be accomplished.

It was found that the tungsten wire was not heated to visible luminosity in the discharge in air, while a platinum wire of the same size was raised to a white heat. Platinum therefore seems to be a catalytic agent for atomic nitrogen, while tungsten is inoperative. I have not yet tried platinum in pure nitrogen, and it may be that the oxygen plays a part in the surface reaction which heats the platinum.

It seems to be now clear why a more complete series of Balmer lines is obtained in the solar corona and probably in nebulæ (provided sufficient exposure were given) than in vacuum tubes. The luminous gases are in these cases not in proximity to catalyzing surfaces, and consequently atomic hydrogen of 100 per cent. concentration can exist. Of course the possibility of a different type of excitation still remains.

To further extend the series in the laboratory, it will probably be necessary to devise a method of more completely poisoning the walls of the tube, or abolish the wall entirely, as can be done perhaps by means of a very powerful discharge of the ring type excited by high-frequency inductive effects, in an electrodeless tube.

Pyrex glass has been found better than soft glass, but quartz appears to be no better than pyrex.

The fact that we have only atomic hydrogen in the central part of a long spectrum tube, even during the brief moments when no current is passing (between the half-cycles), makes it appear probable that the refractive index of the gas in the atomic condition can be determined by introducing the tube into one path of an interferometer, and illuminating the instrument with flashes of light, during the moments when the current is not passing, by means of a disk perforated with two slots rotated by a synchronous motor. This experiment will be tried in the autumn.

Part II. *The Balmer Series.*

In continuing the work on the Balmer spectrum of hydrogen, tubes of pyrex glass have been used exclusively. The aluminium-foil electrodes were attached to tungsten wires, which fuse easily into pyrex. As there is apt to be a slow capillary leak along the tungsten wire, a drop of sealing-wax was always melted around the wire on the outside of the bulb. These tubes, if made of carefully cleaned glass, will come into the "black stage" (showing the Balmer lines on a black background when viewed through a direct-vision prism) after ten or fifteen minutes' operation.

The lines of the Balmer series were photographed in the 2nd- and 3rd-order spectrum of a very perfect 7-inch plane grating (temperature controlled to $0^{\circ}{\cdot}1$ by a thermostat) with an objective of 20-foot focus, H_α, H_β, and H_γ all showing as clearly separated doublets. The series was recorded with this apparatus as far down as the 18th line with an exposure of only 12 hours. Only a few minutes were required for the plates showing H_γ–H_ϵ.

Curtis, using a concave grating of rather short focus, with an exposure of 5 hours obtained only the first six lines of the series. When we consider that the sixth line has an intensity about 4000 times as great as that of the 18th line, the enormous intensity and efficiency of the long end-on tube is at once apparent. The tube was excited by a large 6000-volt transformer.

Photographs were also made in the 5th-order spectrum of a plane grating, in combination with a collimator and Cooke portrait lens of 1-metre focus. A screen of glass coloured by nickel oxide was used to cut out the overlapping green of the 3rd order and violet of 5th order, which covered the region of the last lines of the Balmer spectrum. This glass is opaque to all visible light except the extreme red, and is

highly transparent to the ultra-violet region in the vicinity of the end of the Balmer series.

The grating was selected by illuminating it with the light from a quartz-mercury arc, mounted in a closed box provided with a window of dense nickel-oxide glass. This arrangement gives a powerful beam of radiation of wave-length 3660, which was rendered convergent by a lens and reflected from the grating to a screen of barium platinocyanide.

In this way a grating was found which was enormously bright in the 5th-order spectrum for the region of the end of the Balmer series ($\lambda=3676$).

With this grating and the new tubes of pyrex glass, the 20th line was photographed with certainty, and probably the 22nd line. The 21st is so nearly in coincidence with a strong line of the secondary spectrum that it cannot be identified under present conditions.

H_2 and H_3 were not photographed, as we have Curtis's values, which are of the same order of accuracy as those about to be given.

The plates were measured and the wave-lengths computed by Mr. Arthur E. Ruark, one of my students, to whom I am indebted for a large amount of very faithful and accurate work. The reference iron-lines were the tertiary standards determined by St. John and Babcock *, lines showing no pole effect being used in most cases.

Reduction to vacuum was done by the table of Meggers and Foote †.

Line.	λ (air).	λ (vac.).	Difference between these values and those of Curtis.	
1	*6562·793		0	
2	*4861·326		0	
3	4340·465	4341·681	−0·001	From C.'s observed wave-lengths.
4	4101·731	4102·884	− ·007	
5	3970·073	3971·192	− ·002	
6	3889·064	3890·161	+ ·012	
7	3835·397	3836·481	+ ·010	From C.'s calculated wave-lengths.
8	3797·910	3798·984	+ ·010	
9	3770·634	3771·701	+ ·001	
10	3750·152	3751·214	+ ·002	
11	3734·371	3735·429	·000	
12	3721·948	3723·003	+ ·007	
13	3711·980	3713·032	+ ·007	
14	3703·861	3704·911	+ ·006	
15	3697·159	3698·197	+ ·005	
16	3691·553	3692·600	+ ·004	
17	3686·833	3687·878	− ·001	
18	3682·825	3683·869	+ ·015	
19	3679·372		+ ·015	
20	3676·378		+ ·013	

* Values given by Curtis.

* Astrophys. J. vol. liii. (1921), or Mt. Wilson Contrib. No. 202.

† Bur. of Standards Sci. Papers, No. 327 (1918).

On one of the plates, taken with an exposure of only 5 minutes, H_γ appeared beautifully separated, the distance between the components being fully three times the width of either component. This makes it appear probable that we can resolve also the 4th and possibly the 5th line, by operating the tube with a current of comparatively small intensity.

Two series of measurements, each consisting of fourteen settings on the components of H_γ, gave the following values for the doublet separation :

1st series	·0568
2nd series	·0601
Mean	·0584 I.A.,

which is in exact agreement with the value obtained by Gehrcke and Lau and is ·004 I.A. less than the value given by McLennan and Lowe.

The actual wave-lengths of the components of the doublet H_γ are 4340·494 and 4340·435, the value given in the table being, of course, the centre of the doublet.

I have been aided in this investigation by a grant from the Rumford Fund of the American Academy.

Baltimore, U.S.A.,
June 1st, 1922.

L. *On the Spectra of X-rays and the Theory of Atomic Structure.* *By* D. Coster *.

Part IV.†

New Measurements in the L-*series of the Elements* La (57)–Lu (71).

1. In Part II. of this paper I gave the results of my measurements of the elements Rb–Ba, in this part I will deal with those of the rare-earth metals. As is known, the latter elements are very similar in chemical properties,

* Communicated by Prof. Sir E. Rutherford, F.R.S.
† See Phil. Mag. xliii. p. 1070 (1922), Parts I., II., and III.

and it is rather difficult to get them in a very pure state. Some preliminary investigations with rather impure specimens of these elements showed clearly that from these no certain information could be obtained about the weaker lines, since the great number of "foreign" lines appearing on the plates make the interpretation of the photographs nearly impossible.

The present investigation has been rendered possible by the kindness of Mr. Auer von Welsbach, who offered to this laboratory a beautiful collection of very pure salts of these elements. On the photographs taken with these salts usually no lines were observed belonging to any other rare-earth metal. As the presence of about 0·1 per cent. of another element would be sufficient to give the stronger lines, we may conclude that the salts used were extremely pure. In the one case, however, of Yb (70) several lines were observed belonging to Lu (71).

§ 2. The apparatus was the same as that used for the former work. In this region of wave-lengths the spectrograph need not be exhausted. The slit of the X-ray tube was covered with an aluminium sheet of 10 μ. After being glowed in a Bunsen flame the salts (sulphates) were pressed on a roughened copper or silver plate, which was soldered on the anticathode. Imperial Eclipse plates were used, which appeared to be much more adapted to X-ray work than the technical X-ray plates previously used in this laboratory. These plates are extremely sensitive, especially for wave-lengths of more than 3 Å.U., and even for wave-lengths of 1–2 Å.U. they give better images than the technical X-ray plates in half the time of exposure.

For the rather small glancing angles in question (10–20 degrees) the apparatus seemed in the beginning to be very inconstant, giving sometimes fairly good and sometimes very bad plates. This phenomenon appeared to be connected with the reflexion on different parts of the crystal; very good plates were only obtained if the radiation was reflected by the middle part of the crystal. As it seems to be impossible that this phenomenon should depend on the geometrical conditions of the apparatus we must assume that the reflecting power of the crystal was greatest at the middle part. Once the cause of this phenomenon was known, it was only a matter of time to obtain rather good plates for all the elements, as by a change of the position of the focus spot on

the anticathode the radiation can be directed on any desired part of the crystal. This change of the position of the anticathode spot was easily obtained by a change of the relative position of the anticathode and the hot-wire cathode. The hot wire must be renewed about every 8 hours, and frequently after this operation it was necessary to readjust for the most favourable conditions of reflexion.

The tension on the tube was about 25 k.v., the current was not more than 15 m.a., the time of exposure varying from 10 to 45 minutes. Calcite was used as analysing crystal. Some trouble was caused by the copper K lines and the tungsten L lines, which cannot be avoided when working with a tube of brass and a tungsten hot wire. In a few cases these foreign lines made it impossible to measure some weak lines belonging to the element under investigation.

§ 3. As regards the accuracy of the measurements I may refer to Part II. § 4 of this paper. In general, the lines for the elements La–Lu are much sharper than those for the elements with lower atomic number. On the other hand, most of the stronger lines are accompanied by fairly intense satellites which often lie very close to them, thus diminishing the accuracy of the measurements. Usually the errors in the wave-lengths of the satellites themselves are larger than those in the wave-lengths of the diagram-lines, as the satellites are more diffuse.

With the exception of the lines β_7 and γ_8, which are dealt with in Part IV. § 10, all the diagram-lines (see diagram IV. Part V. § 2) are given in Tables XIII., XIV., and XV. The lines appearing with two decimal places have been taken from Hjalmar's precision measurements*, the other lines having been determined in the present investigation relatively to these lines or to the copper, tungsten, or zinc lines, which also appeared on the plates. For the elements Eu, Gd, and Tb the line η could not be separated from α_1 or α_2, which are much sharper and more intense.

* *Zeitschr. f. Physik*, iii. p. 262 (1920) and vii. p. 341 (1921).

Table XIII.

Wave-lengths in X.U. (10^{-11} cm.).

	l	η	α_2	α_1	β_4	β_1	β_3	β_6	$\beta_{2,7}$	γ_5	γ_1	γ_2	γ_3	γ_4
57 La...	3000	2734	2668·93	2659·68	2443·8	2453·30	2405·3	2373·9	2298·0	2200·8	2137·20	2041·6	2036·6	1978·7
58 Ce ...	...	2614·7	2565·11	2556·00	2344·2	2351·00	2305·9	2276·9	2204·1	2105·6	2044·33	1955·9	1950·9	1895·2
59 Pr ...	2778·1	2507	2467·63	2457·70	2250·1	2253·90	2212·4	2185·9	2114·8	2016·1	1956·81	1875·0	1869·9	1815·3
60 Nd...	2670·3	2404·2	2375·63	2365·31	2162·2	2162·21	2122·2	2099·3	2031·4	1931·3	1873·83	1797·4	1792·5	1740·8
62 Sm..	2477·0	2214	2205·68	2195·01	1996·4	1993·57	1958·0	1942·2	1878·1	1775·1	1723·09	1655·9	1651·7	1603·3
63 Eu...	2390·3	...	2127·33	2116·33	1922·1	1916·31	1882·7	1870·5	1808·2	1705	1654·3	1593·9	1587·7	...
64 Gd...	2307·1	...	2052·62	2041·93	1849·3	1842·46	1810·9	1803·1	1741·9	1637·6	1588·63	1531·0	1525·9	1481·8
65 Tb...	2229·0	...	1982·31	1971·49	1781·4	1772·68	1742·5	1737·5	1679·0	1574·2	1526·6	1473·8	1468·3	1423·9
66 Dy...	2154·0	1892·2	1915·64	1904·60	1716·7	1706·58	1677·7	1677·7	1619·8	1515·2	1469·7	1420·3	1413·9	1371·4
67 Ho...	2082·1	1822·0	1852·06	1840·98	1655·3	1643·52	1616·0	1618·8	1563·7	1459	1414·2	1367·7	1361·3	1319·7
68 Er ...	2015·1	1754·8	1791·40	1780·40	1596·4	1583·44	1557·9	1563·6	1510·6	1403	1362·3	1318·4	1311·8	1273·2
70 Yb...	1890 0	1631·0	1678·9	1667·79	1488·2	1472·5	1449·4	1462·7	1412·8	1303·0	1264·8	1225·6	1219·8	1182·0
71 Lu...	1831·8	1573·8	1626·36	1615·51	1437·2	1420·7	1398·2	1414·3	1367·2	1256	1220·3	1183·2	1177·5	1141·1

Table XIV.

Frequencies in multiples of the Rydberg number (109737 cm.$^{-1}$).

	l	η	α_2	α_1	β_4	β_1	β_3	β_6	β_2	γ_5	γ_1	γ_2	γ_3	γ_4
57 La ...	303·77	333·28	341·43	342·61	372·89	371·44	378·87	383·87	396·55	414·06	426·37	446·36	447·44	460·54
58 Ce ..	...	348·51	355·25	356·51	383·73	387·60	395·18	400·23	413·45	432·77	445·74	465·92	467·10	480·84
59 Pr ...	328·01	363·54	369·28	370·77	404·99	404·30	411·89	416·89	430·89	451·99	465·68	486·02	487·33	501·98
60 Nd ...	341·26	379·03	383·58	385·25	421·44	421·44	429·39	434·09	448·59	471·85	486·30	507·00	508·37	523·48
62 Sm ...	367·89	411·59	413·14	415·14	456·45	457·09	465·41	469·19	485·22	513·36	528·86	550·32	551·71	568·36
63 Eu ...	381·23	...	428·35	430·58	474·11	475·52	484·03	487·18	503·97	534·59	550·85	571·72	573·95	...
64 Gd ...	395·15	...	443·94	446·27	492·76	494·58	503·21	505·39	523·14	556·48	573·60	595·22	597·22	614·98
65 Tb ...	408·83	...	459·69	462·21	511·54	514·05	522·96	524·47	542·74	524·47	596·93	618·30	620·64	639·98
66 Dy ..	423·07	481·59	475·69	478·44	530·83	533·96	543·16	543·16	562·59	601·43	620·02	641·61	644·49	664·46
67 Ho ...	437·68	500·15	492·02	494·98	550·51	554·45	563·90	562·93	582·78	624·67	644·36	666·28	669·42	690·53
68 Er ...	452·22	519·31	508·68	511·82	570·82	575·48	584·93	582·82	603·24	649·70	668·92	691·19	694·67	715·73
70 Yb ...	482·15	558·73	542·76	546·38	612·33	618·85	628·74	622·99	645·00	699·35	720·05	743·51	747·05	770·94
71 Lu ...	497·48	579·04	560·30	564·06	634·07	641·42	651·73	644·33	666·52	725·53	746·74	770·17	773·87	798·60

TABLE XV.

$\sqrt{\frac{\nu}{R}}$ (square roots of the frequencies).

	l	η	α_2	α_1	β_4	β_1	β_3	β_5	β_2	γ_5	γ_1	γ_2	γ_3	γ_4
57 La ..	17·429	18·256	18·477	18·510	19·310	19·273	19·465	19·593	19·914	20·348	20·649	21·127	21·153	21·460
58 Ce ...	...	18·668	18·848	18·882	19·716	19·687	19·879	20·006	20·333	20·803	21·113	21·585	21·613	21·928
59 Pr ..	18·111	19·067	19·217	19·255	20·124	20·107	20·295	20·418	20·758	21·260	21·580	22·046	22·076	22·405
60 Nd ..	18·473	19·469	19·585	19·627	20·529	20·529	20·722	21·073	21·180	21·722	22·052	22·517	22·547	22·879
62 Sm	19·181	20·288	20·326	20·375	21·364	21·380	21·574	21·661	22·028	22·658	22·997	23·459	23·488	23·840
63 Eu ..	19·525	...	20·697	20·750	21·774	21·806	22·001	22·072	22·449	23·121	23·470	23·911	23·957	...
64 Gd ..	19·878	...	21·070	21·125	22·198	22·239	22·432	22·481	22·872	23·590	23·950	24·397	24·438	24·799
65 Tb ...	20·220	...	21·440	21·499	22·617	22·673	22·868	22·901	23·297	24·060	24·432	24·866	24·913	25·298
66 Dy ..	20·569	21·945	21·810	21·873	23·040	23·108	23·306	23·306	23·719	24·524	24·900	25·330	25·387	25·777
67 Ho...	20·921	22·364	22·182	22·248	23·463	23·549	23·747	23·726	24·141	24·993	25·385	25·812	25·873	26·278
68 Er ...	21·265	22·788	22·554	22·624	23·892	23·989	24·185	24·142	24·561	25·489	25·863	26·291	26·357	26·753
70 Yb ..	21·958	23·637	23·297	23·375	24·745	24·877	25·075	24·960	25·397	26·445	26·834	27·267	27·332	27·766
71 Lu ..	22·304	24·063	23·671	23·750	25·181	25·326	25·529	25·384	25·817	26·936	27·327	27·752	27·819	28·259

§ 4. The classification of the lines proposed in this paper is strongly supported by Tables XVI. and XVII. Table XVI. gives the relativity L-doublets. From this table we

TABLE XVI.

Relativity L-doublets.

	$\eta-l$	$\beta_1-\alpha_2$	$\gamma_5-\beta_8$	$\gamma_1-\beta_2$	$\gamma_9-\beta_{14}$	L_2-L_1
57 La	29·51	30·01	30·19	29·86	...	...
58 Ce	...	32·35	32·54	32·29	32·42	32·50
59 Pr	35·53	35·02	35·10	34·79	34·80	35·24
60 Nd	37·77	37·86	37·76	37·71	37·67	37·94
62 Sm	43·70	43·95	44·17	43·64	43·62	...
63 Eu	...	47·17	47·41	46·88	47·10	...
64 Gd	...	50·64	51·11	50·46	50·83	...
65 Tb	...	54·36	54·43	54·19	54·32	...
66 Dy	58·52	58·27	58·27	57·43	...	...
67 Ho	62·48	62·43	61·74	61·58	62·08	...
68 Er	67·09	66·80	66·88	65·68	..	...
70 Yb	76·58	76·09	76·36	75·05	...	...
71 Lu	81·56	81·12	80·88	80·22	...	...
73 Ta	93·33	92·68	91·99	91·64	...	...
74 W	98·76	98·54	99·00	98·05	...	...

TABLE XVII.

Differences in $\sqrt{\frac{\nu}{R}}$.

	$\beta_4-\eta$	$\beta_3-\beta_1$	$\gamma_2-\gamma_5$	$\gamma_3-\gamma_1$
57 La	1·054	0·192	0·779	0·504
58 Ce	1·048	·192	·782	·500
59 Pr	1·059	·192	·786	·496
60 Nd	1·060	·193	·795	·495
62 Sm	1·076	·194	·801	·491
63 Eu	...	·195	·790	·487
64 Gd	...	·193	·807	·488
65 Tb	...	·195	·806	·481
66 Dy	1·095	·198	·806	·487
67 Ho	1·099	·198	·819	·488
68 Er	1·104	·196	·802	·494
70 Yb	1·108	·198	·822	·498
71 Lu	1·118	·202	·816	·492
73 Ta	1·119	·204	·848	·494
74 W	1·136	·202	·822	·483
83 Bi	1·200	·224	·910	·495

may conclude that the frequency difference $\gamma_1-\beta_2$ is essentially smaller than the other doublet differences *. As the

* Compare Part II, § 5 of this paper. See also D. Coster, *Zeitschr. f. Physik*, vi. p. 185 (1921), table 3.

lines γ_1 and β_2 were usually measured only by reference to other lines this table is not very well adapted for an accurate calculation of the energy difference between the N_4 and N_3 level (see diagram IV.). The lines γ_9 and β_{14} are dealt with in § 11 of Part IV. The last column gives the frequency difference between the absorption discontinuities L_1 and L_2 as measured by the author.

Table XVII. gives those differences of the square roots of the frequencies, which according to Part II. § 5 are nearly constant. As the absolute errors in the frequencies are about inversely proportional to the second power of the corresponding wave-length, it is scarcely surprising that there are more irregularities in this table than in the corresponding Table V.

§ 5. In Table XVIII. the L absorption discontinuities of some of the elements are given. They were found on the same plates where the emission-lines were photographed

TABLE XVIII.

Absorption discontinuities.

	Wave-lengths.		Frequencies.	
	L_1	L_2	L_1	L_2
58 Ce	2159·7	2005	421·94	454·44
	(2158)	(2007)	(422·3)	(454·0)
59 Pr	2072·7	1919·7	439·44	474·68
	(2071)	(1922)	(440·0)	(474·1)
60 Nd	1990·3	1837·6	457·86	495·90
	(1992)	(1842)	(457·5)	(494·7)
62 Sm.....	1840·9	...	495·02	...
63 Eu.....	1773	...	514·07	...

(compare Part II. § 9), and were measured relatively to β_2 or γ_1 of the same element. Hertz's values are added in parentheses; they agree better with ours for the elements Ce, Pr, and Nd than for Ba and Cs * (see Tables XI. and XII. Part II. § 9). Absorption-discontinuities may be measured very easily in this way, but the method is only applicable if

* It may be stated that my values for the latter elements agree very well with those of Mr. Lindsay (compare Part III. § 8).

no emission-lines are found in the same place, and, again, it seems to be only suitable for a definite range of wave-lengths.

§ 6. The faint lines lying on the short wave-length side of β_2 gave a great deal of trouble. The photographs of the elements W, Ta, and Lu, as well as those of the elements Sb–Ag, showed that we have to expect 4 or 5 lines in this region. For the elements Er–Sb, however, these lines lie very near to one another (they all fall in a length of less

TABLE XIX.

Wave-lengths.

	β_7	β_9	β_{10}	β_{11}	β_{12}
47 Ag	(β_2)	3620	3630	3663·3	3653·7
48 Cd	,,	...	....	3477·5	3468·4
49 In	3317	3259·8	3265·8	3304·0	3295·9
50 Sn	3149	3108·1	3114·4	3142·6	3134·7
51 Sb	(β_{11})	2965·8	2972·5	2993·4	2985·8
55 Cs	2480	2473	β_7	2483	
56 Ba	2375·6	2371·2	...	2381·7	
57 La	2270	2277	2285	(β_9, β_{10})	
58 Ce	2176·3	2184·0	2191·6	,,	
59 Pr	2087·4	2095·8	2102·5	,,	
60 Nd	2004·3	2011·7	2019·3	,,	
62 Sm	1852·3	1858·1	1865·7	(β_{10})	
63 Eu	1784	1788	1796	,,	
64 Gd	1719·6	(β_7)	1728·1	,,	
65 Tb	1655·8	,,	1664	,,	
66 Dy	1595·7	,,	...	...	
68 Er	1489·2	1482·3	(β_7)	1501·4	
71 Lu	1345·9	1333·0	1339·8	1359	
73 Ta	1260·0	1242·9	1250·6	1273·8	
74 W	1220·8	1202·1	1209·4	1235·4	

than 1 mm. of the plate), so that we may assume that they must coincide or cross in several cases. This made the classification of the lines a very complicated puzzle. Several solutions of it have been tried, that which seems to be the best is given in Tables XIX. and XX.

The following facts support this classification. It has been assumed that the line β_5 does not occur in this region under the conditions of the experiments, for the following reasons. For the elements in the neighbourhood of W it was shown * that β_5 and the L_1 discontinuity nearly coincide. For the elements from Eu (63) to Cs (55) the L_1 absorption discontinuity was obtained on the plate as a white line on a

* D. Coster, Phys. Rev. xix. p. 20 (1922).

dark background. No indication of an emission-line which could be β_5 was found for these elements. Interpolating between the values of β_5 for W and Ta and the L_1 discontinuities of Eu–Ba we get values which do not coincide with a measured line for any of the elements Lu–Gd. Only in the case of Tb (65) a very faint discontinuity in the blackening of the plate was observed at about 1647 X.U., a value which agrees very well with the interpolated value; but this discontinuity in the blackening looked more like an

TABLE XX.

Frequencies.

	β_7	β_9	β_{10}	β_{11}	β_{12}	$\beta_4-\beta_{10}$	$\alpha_1-\alpha_2$
47 Ag ...	(β_2)	251·67	251·05	248·76	249·40	0·62	0·43
48 Cd ...	,,	...	...	262·05	262·73	...	0·50
49 In ...	274·73	279·55	279·03	275·81	276·48	0·52	0·57
50 Sn ...	289·37	293·19	292·60	289·97	290·69	0·59	0·62
51 Sb ...	(β_{11})	307·26	306·57	304·43	305·20	0·69	0·69
55 Cs ...	367·38	368·58	β_7	367·00		1·20	1·04
56 Ba ...	383·60	384·31	...	382 62		...	1·11
57 La ...	401·41	400·23	398·87	(β_9, β_{10})		1·36	1·18
58 Ce ...	418·73	417·25	415·80	,,		1·45	1·26
59 Pr ...	436·56	434·80	433·42	,,		1·38	1·49
60 Nd ...	454·65	452·99	451·29	,,		1·70	1·67
62 Sm ...	491·96	490·44	488·42	(β_{10})		2·02	2·00
63 Eu ...	510·76	509·78	507·31	,,		2·47	2·23
64 Gd ...	530·22	(β_7)	527·32	,,		2·61	2·33
65 Tb ...	550·34	,,	547·63	,,		2·71	2·52
66 Dy ...	571·09	,,	...	...		...	2·75
68 Er ...	611·91	614·69	(β_7)	606·96		2·78	3·14
71 Lu ...	677·07	683·63	680·15	670·61		3·48	3·76
73 Ta ...	723·30	733·22	728·65	715·60		4·57	4·37
74 W ...	746·45	758·06	753·50	737·60		4·56	4·60

absorption edge than a line, whereas the line β_5, though very faint, for W and Ta is still a very sharp line.

§ 7. The line β_7 follows Moseley's law closely. Furthermore, the behaviour of this line is what we should expect from theoretical considerations (compare Part V. § 2). For Cd and Ag it could not be separated from the broadening on the short wave-length side of β_2, but, since for Ag and especially for Cd this broadening extends to a larger region and is more sharply limited than for the other elements in the neighbourhood, we may assume that β_7 exists also for these elements.

§ 8. The lines β_9 and β_{10} were studied by the author in a former paper *. They are both very faint lines, β_{10} is still

* *Zeitschr. f. Physik*, vi. p. 185 (1921).

weaker than β_9. They seem to correspond to transitions which are inconsistent with the rules of selection given in Part I. § 3. β_9 should correspond to the transition M_1–L_3, β_{10} to the transition M_2–L_3. From this we must expect that the frequency difference of these lines is equal to the frequency difference $L\alpha_1$–$L\alpha_2$. Both differences are given in the last columns of Table XX. They agree within the limits of experimental error. Further, we must expect the following relation to hold for the frequencies :

$$L\beta_9 = L\alpha_1 + L_3 - L_1,$$

where L_1 and L_3 are the first and third absorption discontinuities in the L-series. In Table XXI. the frequencies

Table XXI.

Frequency of β_9.

	Calculated.	Measured.
47 Ag	251·95	251·67
48 In	279·57	279·55
50 Sn	293·12	293·19
51 Sb	307·39	307·26
55 Cs	368·36	368·58
56 Ba	384·82	384·31
58 Ce	417·4	417·25
59 Pr	435·3	434·80
60 Nd	453 3	452·99
62 Sm	490·5	490·44
74 W	757·52	758·06

calculated in this way are compared with the experimental values. The absorption edges of Ag have been taken from Part I. § 9, Table XII., the edges for Sb, Cs, and Ba have been taken from measurements by Mr. Lindsay, those for W from Duane and Patterson. For In and Sn the frequency difference γ_4–β_7 has been taken, which for these elements must be nearly the same as L_3–L_1 ; for Cd, Pr, Nd, and Sm, L_1 has been taken from the author's measurements (see Table XVIII.) ; whereas the value for L_3 for these elements has been calculated from γ_4 (it has been assumed that for these elements the frequency difference L_3–γ_4 is 2 units). As is seen from the table the agreement between the measured and calculated values is very good.

§ 9. The lines β_{11} and β_{12} have recently been measured by the author for the elements Nb–Sb (see Part II. Table X.).

For the elements Mo–In they are fairly intense lines, but they are not very sharp: their intensity seems to decrease rather rapidly for elements with higher atomic number than In. As has been pointed out in Part II. § 8, the frequency differences β_{11}–β_2 and β_{12}–β_2 vary linearly with the atomic number. If we assume, as has been done by Dauvillier * and Wentzel †, that the line β_5, found for a great number of the elements Ta–U ‡ is a double line, it is very probable that this line is the same as the lines formerly denoted as β_{11} and β_{12} for the elements with lower atomic number. The variation in intensity of these lines, however, is very remarkable. As has been stated above, their intensity relative to that of the other lines is decreasing for the elements with higher atomic number than In: for the elements in the neighbourhood of W these lines are extremely faint, whereas their intensity seems to increase again for the elements in the neighbourhood of Au. Besides, their frequency difference with the lines β_2 seems to vary for the heaviest elements more rapidly than with the first power of the atomic number. This made it somewhat difficult at first to recognize the line β_5 of the heaviest elements in the lines β_{11} and β_{12} for the elements Nb–Sb.

Where two lines were expected nearly to coincide, in most cases a broadening or darkening of the measured line was actually observed. In this case the wave-length given is only a mean value. In Tables XIX. and XX. this value stands in the column of the line which was considered to be the most intense of the two coinciding lines. For Ho (67) and Yb (70) the lines in question could not be measured, as in this region copper K lines appear. It may be pointed out that in general for the elements of Tables XIX. and XX., with the exception of some copper and tungsten lines, no other lines were found on the short wave-length side of β_2 other than the lines appearing in the tables.

§ 10. Table XXII. gives two very weak lines, which were only found for some elements where very good plates were obtained. γ_7 is a non-diagram line, formerly given for the elements Mo–Ba (Table X., Part II.); γ_8 is a diagram line, representing the transition O_3–L_2. As is seen from the table the frequency difference $L\gamma_8$–$L\beta_7$ is equal to $L\beta_1$–$L\alpha_2$ within the limits of experimental error. The line γ_8 was

* Dauvillier, *Comptes Rendus*, clxxiii. p. 647 (1921).

† Wentzel, *Ann. d. Physik*, lxvi. p. 437 (1921).

‡ D. Coster, *Zeitschr. f. Physik*. l. c.; Dauvillier, l. c. (Dauvillier calls this line β_2'').

TABLE XXII.

	Wave-lengths.		Frequencies.			
	γ_7	γ_8	γ_7	γ_8	$\gamma_8-\beta_7$	$\beta_1-\alpha_2$
56 Ba	2218	2218	410·82	410·82	27·22	27·74
58 Ce	2029	2019	449·22	451·24	32·51	32·35
59 Pr	1942·2	1932·2	469·20	471·62	35·06	35·02
60 Nd	1859	...	490·20	...	...	...
63 Eu	1644	1629	554·18	559·23	48·47	47·17
71 Cp	1211	1202	752·32	758·02	80·96	81·12
73 Ta	...	1117	...	815·83	92·53	92·68
74 W	...	1079	...	844·56	98·11	98·54

never observed by the author for elements with higher atomic number than 74. γ_7 is not only an extremely weak, but also a rather diffuse line, which for the heavier elements lies rather close to the very intense line γ_1. This makes it nearly impossible to be sure of the existence or non-existence of this line for the heaviest elements.

§ 11. Tables XXIII. and XXIV. give some lines denoted as β_{14}, γ_9, and γ_{10}, which were only observed in the region of the rare earth metals. Their appearance seems to be connected with the change in the N-shell of the atom, which we must expect in this region according to Bohr's theory (compare Part III. § 8). For Ba the lines β_{14} and γ_9 do not exist, neither were they observed for La, but here the plates

TABLE XXIII.

Wave-lengths.

	β_{14}	γ_9	γ_{10}	β_{13} (?)
55 Cs	...	...	2236·9	...
56 Ba	...	...	2140·2	...
57 La	...	...	2048·1	...
58 Ce	2212·1	2051	1962·3	...
59 Pr	2122·0	1962·2	1881·1	...
60 Nd	2038·8	1880·4	1802·2	...
62 Sm	1885·1	1728·5	1659·3	1987·1
63 Eu	1781·4	1659·3	...	1909·2
64 Gd	1748·1	1593·6	...	1835·5
65 Tb	1685·1	1531·4	...	1765·5
66 Dy	1625·1	...	...	1699·2
67 Ho	1567	1416	...	1635·5
68 Er	1512	...	...	1575·6

TABLE XXIV.

Frequencies.

	β_{14}	γ_9	γ_{10}	$\beta_2-\beta_{14}$	$\gamma_1-\gamma_9$	$\gamma_2-\gamma_{10}$
55 Cs	...	...	407·39	...	...	0·84
56 Ba	...	...	425·78	...	...	1·25
57 La	...	...	444·92	...	...	1·44
58 Ce	411·95	444·37	464·39	1·50	1·37	1·44
59 Pr	429·43	464·42	484·44	1·45	1·26	1·53
60 Nd	446·96	484·63	505·64	1·63	1·67	1·58
62 Sm	483·40	527·20	549·20	1·82	1·66	1·12
63 Eu	502·08	549·18	...	1·89	1·67	...
64 Gd	521·25	572·08	...	1·89	1·52	...
65 Tb	540·77	595·09	...	1·97	1·84	...
66 Dy	560·76	...	...	1·83	...	...
67 Ho	581·48	643·56	...	1·50	0·80	...
68 Er	602·70	...	...	0·54	...	...

were not especially good. For Ce they are very weak, lying on the long wave-length side of β_2 and γ_1. From Ce down to Tb they get more intense (for Tb they are of about the same intensity as β_4) at the same time as their frequency difference with the lines β_2 or γ_1 slowly increases. For the elements with higher atomic number than Tb, these differences rapidly decrease, whereas their intensity relatively to the other lines remains nearly the same. For the elements Ho and Er they could not wholly be separated from β_2 and γ_1: for these elements the values of their wave-lengths were roughly calculated from the broadening of β_2 and γ_1. For Yb (70) and Lu (71) β_{14} and γ_9 had wholly disappeared. For Dy β_{14} could not be observed, as for this element the tungsten $L\alpha_1$ line was appearing on the long wave-length side of β_2. As is seen from Table XXIV., the frequency difference $\gamma_1-\gamma_9$ seems to be somewhat smaller than the difference $\beta_2-\beta_{14}$.

A very remarkable line is γ_{10}, which appeared for the first time for Cs at the long wave-length side of γ_2. It is a rather intense line, being more sharply limited on its short wave-length side than on the other side. As is shown in Table XXIV. its frequency difference from γ_2 increases first with increasing atomic number, but for elements with higher atomic number than Nd the same difference rapidly decreases, so that this line could not be separated from γ_2 for elements with higher atomic number than Sm. But up to Er (68) γ_2 was somewhat broadened and diffuse on the long wave-length side, indicating that also for these elements γ_{10} is still present. For the elements Nd–Cs, where γ_{10} was wholly separated from γ_2, the latter line appeared to be a faint, but

fairly sharp line. Since in the elements Ta–Er, for which γ_{10} is not present, a change in the relative intensity of γ_2 was already observed, it appears that this change in intensity cannot be interpreted as being connected with the presence of γ_{10}. For Te and the elements with lower atomic number γ_2 can no longer be separated from γ_3. It is difficult to say whether γ_{10} still exists for these elements or not, but it seems to be hardly probable.

For the elements Sm–Eu a faint line was observed on the short wave-length side of β_1. The presence of β_4 in this place made it impossible to study this line for the elements with lower atomic number than Sm. and in the same way the presence of β_6 made measurements impossible for elements with higher atomic number than 68. It may be that this line is the same as β_{13} previously measured for the elements Rb–Sb—its wave-lengths are given in Table XXIII.

Part V.

Comparison of the new Experimental Results with Bohr's Theory.

§ 1. The L-series of most of the elements from Rb (37) to U (92) has now been thoroughly investigated by the author*, working in the laboratory of Prof. Siegbahn: and from this work it appears that the same simple laws which have been dealt with in Part I. govern the emission of the X-ray spectra of the elements from U down to Rb. There are still some lacunæ in my tables, but these have no particular meaning, as it should only be a matter of patience and time to fill them. Some rather faint lines were overlapped by sharper and more intense lines of the same or another element, making measurement very difficult. Of some elements no suitable specimens were available, some elements gave difficulties due to their high vapour pressure. In this connexion it may be pointed out that the L-spectrum of mercury has been measured in a very ingenious way by Mr. Müller†; most of his results agree very well with ours.

The L-spectrum of tungsten has been measured by several authors with essentially the same results. In addition, Dauvillier ‡ has measured the L-spectrum of U, Au, Pt, Ir,

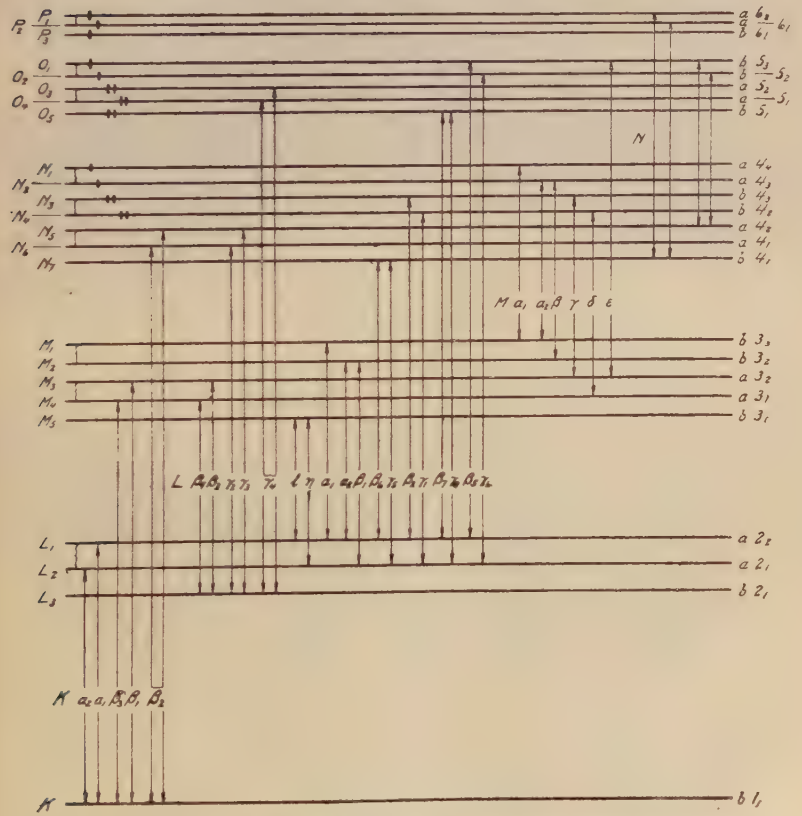
* As has been stated above, for the measurements of the elements Rb–Ta, use was made of the precision measurements of the strongest lines of these elements done by Hjalmar, and for W Siegbahn's precision measurements were used. For the wave-length tables of Ta–U, see D. Coster, *Zeitschr. f. Phys.* vi. p. 185 (1921).

† Müller, Phil. Mag. xlii. p. 419 (1921).

‡ Dauvillier, *Comptes Rendus*, clxxiii. pp. 647, 1458 (1921).

and Os, and in the lighter elements Sb and part of the Ce-spectrum. In many respects his results agree very well with ours; there are, however, also some important divergences*. It seems to me that, in general, Mr. Dauvillier attaches too much importance to some lines, which he could only establish for one or for very few elements.

Diagram IV.—Niton, Xenon, and Krypton.



§ 2. In Parts I. and III. the level diagrams for niton, xenon, and krypton have been given. These constitute a summary of the measurements, giving at the same time an idea of the successive development of the shells of electrons according to Bohr's theory.

Diagram IV. represents a combination of these former diagrams. The line γ_8, which now has been established for

* Compare D. Coster, *Comptes Rendus*, clxxiv. p. 378 (1922).

7 elements (see Table XXII.) has been added, besides some of the lines belonging to the N-series which has recently been detected by Mr. Dolejsek * in this laboratory have been added. The levels falling out between niton and xenon are denoted in the figure with one dash, those which fall out between xenon and krypton with two dashes. The diagrams I, II., and III. have been thoroughly discussed in Part III., where a comparison of the experimental results and the theory has been given. Here will only be added something in connexion with the line $L\beta_7$, which has now been measured for a great number of elements. This line is for all elements rather faint, and becomes still fainter for the elements with lower atomic number than Ba (56). As has been stated in Part IV. § 7, for the elements with lower atomic number than Ag, it could not be separated from β_2, which for these elements has nearly the same wave-length as the L_1-absorption edge.

Table XXV.

Frequencies.

	$L\beta_7$	$L\alpha_1+M\alpha_1$	L_1	Δ_1	Δ_2
66 Dy.....	571·09	574·27	(574·56)	3·18	(0·29)
68 Er.....	611·91	615·73	(617·03)	3·81	(1·30)
71 Lu.....	677·07	680·62	(683·30)	3·55	(2·68)
73 Ta.....	723·30	726·12	728·65	2·82	2·53
74 W	746·45	749·14	750·85	2·69	1·71
78 Pt.....	844·93	846·76	851·28	1·83	4·52
79 Au.....	870·77	872·13	877·64	1·36	5·51
81 Tl	922·64	923·63	932·16	0·99	8·53
82 Pb.....	950·22	950·26	959·54	0·04	9·28
92 U	1238·14	1236·80	1263·20	−1·34	26·40

Table XXV. gives the frequencies of the line $L\beta_7$ for the elements Dy–U, and in the second column the sum of the frequencies of the $L\alpha_1$ and the $M\alpha_1$ line. The third column gives the absorption-edge L_1. For W to U Duane and Patterson's values are used, for Ta I have used my value of β_5, which must have nearly the same value as L_1, for Lu, Er, and Dy the values for L_1 have been interpolated. Of course, we cannot draw any certain conclusions from the last values, but still it seems to me very improbable that the frequencies of L_1 for Lu, Er, and Dy should be appreciably

* Dolejsek, 'Nature,' cix. p. 582 (1922).

larger than the values given in the table. The last columns give the differences :—

$$\Delta_1 = (L\alpha_1 + M\alpha_1) - L\beta_7 \text{ and}$$
$$\Delta_2 = L_1 - (L\alpha_1 + M\alpha_1).$$

As may be seen from diagram IV., Δ_1 represents the energy difference between the O_5 and the N_1 level. For the elements with lower atomic number than Pb the N_1 level appears to lie higher than the O_5 level, the difference between these levels increasing with decreasing atomic number. As one unit of the frequency, *i.e.*, the Rydberg number, corresponds to 13·45 volt, we may conclude that for Lu, Er, and Dy the N_1 level lies about 45 volt higher than the O_5 level.

Δ_2 represents the binding energy of the 4_4 electron (see diagram IV.). The discontinuity appearing in the table for the value of Δ_2 for W is not essential. Using the author's value of β_5 for L_1 of this element, instead of Duane's and Patterson's value for L_1, we get for W : $\Delta_2 = 2{\cdot}42$, a value which agrees fairly well with the values for the other elements standing in the table. It appears from the table that it is most probable that for Dy the binding energy of the 4_4 electron at least must be less than 20 volt, thus being of about the same magnitude as the binding energy of the valency electrons.

As to the binding energy of the 5_1 electrons, we have to consider two values : one corresponding to the O_5 level and one corresponding to the O_4 level. As may be seen from the table, the first value is at least more than 45 volts for Dy, the second value is given approximately by the frequency difference of the L_3 absorption-edge and the line $L\gamma_4$. From a discussion in Part III. § 8 it follows that the latter difference is likely to be more than 25 volts for Dy. From this we see that, where the 4_4 electrons appear for the first time in the periodic table, they are more loosely bound than the 5_1 electrons ; for the elements with higher atomic number than Pb, however, the 4_4 electrons are definitely bound more firmly than the 5_1 electrons.

§ 3. It is of interest to consider other regions in the periodic system where we might expect to meet with phenomena analogous to those discussed in the last paragraph. In the neighbourhood of the iron group the M-shell develops from a shell containing four 3_1 electrons and four 3_2 electrons into a shell containing six 3_1, six 3_2, and six 3_3 electrons. When the 3_3 electrons appear for the first time, some electrons of the N-shell are already present. Numerical

data about the binding of the 3_3 electrons in this region can only be obtained for Cu and Zn, for which elements the M-shell even has been completed. For this purpose we may compare the frequency of the line $K\beta_2$ with the sum of the frequencies of $K\alpha_1$ and $L\alpha_1$. They are given in Table XXVI.

TABLE XXVI.

Frequencies.

	$K\beta_2$.	$K\alpha_1+L\alpha_1$.
Cu.....	661·30	661·24
Zn.....	709·87	710·89

The values for the K-lines have been taken from the new measurements of Siegbahn and Dolejsek *, the $L\alpha_1$ line has been determined by Hjalmar. This table shows that the binding energy of the 3_3 electron for these elements is not much different from that of the electrons which are present in the N-shell.

For Ag the N-shell has been completed for the first time into a shell of three subgroups of 6 electrons each and respectively with the quantum symbols 4_1, 4_2, and 4_3. From a comparison of the L_1-absorption edge and the line $L\beta_2$ it appears that for this element the binding energy of the 4_3-electron is not more than 10 volts, thus being of about the same magnitude as the energy of the 5-electron which is already present. For the elements with higher atomic number, however, the binding energy of the 4_3-electron increases more rapidly than that of the 5_1-electron.

In the same way it appears from a comparison of the frequencies of the line $L\beta_5$ and the absorption edge L_1 for Au, where according to Bohr the O-shell even has been completed into a shell containing six 5_1, six 5_2, and six 5_3-electrons, that for this element the 5_3-electrons are bound with nearly the same energy as the 6_1-electron.

In this connexion it may be pointed out that the rare-earth metals form a particular group of elements which in certain respects has no analogy in the periodic system. In fact, as the N-shell develops from a shell of three subgroups, each of six electrons, with the quantum symbols 4_1, 4_2, and 4_3 into a shell of four subgroups, each of eight electrons, with the quantum symbols 4_1, 4_2, 4_3, and 4_4, the O-shell has already a certain completion, which was first

* Siegbahn and Dolejsek, *Zeitschrift für Physik*, x. p. 159 (1922).

reached for the rare-gas Xe containing a subgroup of four 5_1 electrons and a subgroup of four 5_2 electrons. For the other regions of the periodic system, however, where, according to Bohr, an inner shell of electrons is being completed (in the neighbourhood of the iron group, of the palladium group, and of the platinum group) no other shell with higher total quantum number than the shell in question has reached a stage of completion.

§ 4. The new measurements of Siegbahn and Dolejsek in the K-series* show that for the elements with lower atomic number than 18 there seems to be some irregularity in the relation of the frequency of the line $K\beta_1$ to the atomic number. This irregularity has been connected with the development of the M-shell. For the elements in the neighbourhood of the iron group, however, where the second stage of this development takes place, no such irregularity was observed. It could perhaps be supposed that there should exist such irregularities for the lines $L\beta_2$, $L\gamma_1$, $L\gamma_2$, and $L\gamma_3$ in the region of the rare-earths, and that the appearance of the satellites on the long wave-length side of these lines should be connected with this fact. Extrapolating these lines, however, from the values for the elements which either precede or follow the rare-earths in the periodic table, we get in both cases values which agree fairly well with those of the measured lines, and at any rate agree much better with those than with the values for the satellites. If there are some irregularities in this region—as we should expect from what has been said about the binding energy of the 4_3-electrons (Part III. § 8)—they must lie within the limits of experimental error. In this connexion, however, it would be of interest to measure the lines β_2, γ_1, γ_2, and γ_3 for the rare-earth metals and for the elements in the neighbourhood of this group with the method of high precision recently developed by Prof. Siegbahn. Unfortunately, this would be very expensive work.

§ 5. As has already been stated in Part III. § 8, it may be assumed that the remarkable satellites, β_{14}, γ_9, and γ_{10}, dealt with in Part IV. § 11, are connected with the completion of the inner N-shell. A possible explanation of these lines is suggested in Part V. § 9. Here I shall only consider certain special points. Though the satellites on the short wave-length side of β_2 and γ_1 (*i.e.*, β_{11} and β_{12} and γ_7) are very faint for the region Ba–Lu, and though they are partly overlapped by other lines, we may conclude, from a thorough examination of the plates, that there is not the

* Siegbahn and Dolejsek, *loc. cit.*

slightest indication of anomalies in this region for these satellites. Therefore, we may assume that there exists no simple numerical relation between the satellites on the long wave-length side and those on the short wave-length side of β_2 and γ_1.

It is difficult to say whether the line denoted as γ_{10} should be connected with γ_2 or with γ_3. As γ_{10} gets closer to γ_2 for elements with higher atomic number than Nd, and finally coincides with this line without crossing it, we are inclined to assume that γ_{10} is only connected with γ_2.

We might expect to meet such anomalous satellites as those described in this paragraph in other regions of the periodic system where an inner shell of electrons is being completed. Thus, in the case of the elements in the region of the palladium group, we should expect anomalies for $L\gamma_{2,3}$, $L\beta_2$, and $L\gamma_1$, and for $K\beta_2$. The authors who have investigated the K-lines in this region do not mention any anomaly for $K\beta_2$. This line, however, is very faint. As to $L\gamma_{2,3}$, it might be that the lines $\lambda=3651$ and 3631 for Rh and $\lambda=3450$ and 3433 for Pd are such anomalous satellites of $\gamma_{2,3}$ (compare Part III. § 5); but they lie on the short wave-length side of this line. For the lines $L\beta_2$ and $L\gamma_1$ in this region no new satellites have been found up to the present. It should, however, be worth while investigating this region again with quartz * as analysing crystal, making use of the Imperial Eclipse photographic plates.

Further, we might expect anomalous satellites in the region of the iron group, where, according to Bohr, the M-shell develops from a shell containing four 3_2 electrons into a shell containing six 3_1, six 3_2, and six 3_3 electrons. In this region Hjalmar † actually observed a satellite on the long wave-length side of $K\beta_1$, which he denoted as β'. Wentzel ‡ has already suggested that the appearance of this line should be connected with the development of the M-shell. In their recent paper Siegbahn and Dolejsek observe that this line is much broader than the breadth of the slit of the spectograph, and that it was not possible to separate this line from $K\beta_1$. From this and from the theoretical interpretation of this line (see Part V. § 9) we might conclude that it is hardly probable that this line is

* As has been pointed out by Prof. Siegbahn, the grating constant of this crystal lies between those of gypsum and calcite, making it especially adapted for the region of wave-length in question.

† Hjalmar, Phil. Mag. xli. p. 675 (1921).

‡ Wentzel, *Annalen d. Physik*, lxvi. p. 437 (1921).

identical with the line denoted by Hjalmar as β_3 for the elements Mg–S, as has been supposed by Sommerfeld *.

Anomalies in the region of the platinum group, which we might expect for the lines $L\beta_5$, $L\gamma_6$, $L\gamma_4$, and perhaps also for the line $L\beta_7$, have as yet not been established. Only the line $L\beta_7$ seems to be a double line in this region. As, however, for the corresponding line $L\beta_6$ in the region of the rare-earth metals no anomalies were observed, it is hardly probable that this structure of β_7 should be connected with the development of the O-shell.

§ 6. As has been stated at the end of Part III., most of the non-diagram lines lie on the short wave-length side of an intense diagram line, their frequency difference with this line being approximately proportional to the atomic number. Moreover, it was suggested that these lines might be emitted by an atom which had lost more than one electron.

In the meantime, a very interesting paper has been published by Mr. Wentzel †, in which he treats the non-diagram lines of the X-ray spectrum. In this paper Mr. Wentzel was able to show that the lines measured by Hjalmar on the short wave-length side of the $K\alpha_1$ line for the lightest elements are emitted by atoms which have lost more than one electron, and he could account in a very suggestive way for the simple numerical relations which hold for the frequencies of these satellites, and for the order of magnitude of the frequency differences of the satellites and the diagram-lines with which they are connected.

In the further elaboration of his theory, however, and especially in the part of his paper dealing with the fine structure of the absorption discontinuities, Mr. Wentzel has made some assumptions which seem to be rather unsatisfactory from a theoretical point of view ‡. In Part III. § 9 of this paper I suggested that under certain conditions the atom might lose more than one electron at the same time by an impact with one single high-speed β-particle, and that the regeneration of such an atom should be accompanied by the emission of a line, which should lie at the short wave-length side of an ordinary diagram-line. Mr. Wentzel, however, supposes that the electrons of double or threefold "ionized" atoms have been removed one by one, thus assuming that the atom, which has already lost one or more electrons, remains

* Sommerfeld, *Zeitschrift f. Physik*, v. p. 1 (1921).

† *Annalen d. Physik*, l. c.

‡ Mr. Rosseland, who first called my attention to this fact, will soon give a theoretical discussion of the problem.

in this state long enough to be deprived of one electron more, before its regeneration takes place.

§ 7. As this point is of fundamental importance for the understanding of the laws which govern the constitution of the atom, I have tried to get some experimental information about this question. Though the experiments have only recently been started, the results hitherto obtained seem to be inconsistent with the assumption of the *successive* ionization of the inner shells of the atom. As has already been pointed out by Mr. Wentzel himself, from his theory we might expect that the intensity of the lines which are emitted by double ionized atoms should increase with the second power of the intensity of the corresponding ordinary diagram-lines.

In Part II. § 7 the satellites of the lines $L\alpha_1$ and $L\beta_1$ have been discussed. It was shown that for Ag and the elements with lower atomic number, the satellites of α_1 have a rather complicated structure. This line seems to be accompanied on the short wave-length side by an emission-band and two rather sharp lines. With the new photographic plate I was able recently to establish a third very faint line of still shorter wave-length than the line denoted as α_1.

After some preliminary examinations five photographs were taken of the $L\alpha$ lines of silver under the same condition as regards position of the crystal, but under the following different conditions :—

	Tension.	Current.	Time of exposure.
Plate I.	9 mm. spark gap.	20 m.a.	3 minutes.
,, II.	8000 volts.	40 ,,	40 ,,
,, III.	8000 ,,	10 ,,	80 ,,
,, IV.	4700 ,,	20 ,,	2½ hours.
,, V.	9 mm. spark gap.	20 ,,	1½ minutes.

For the Plates II., III., and IV. the tension was read with a Braun electrometer giving the mean tension on the tube.

No appreciable difference was found for the Plates I., II., and III. This means that in the case of Plate II., the radiation being about 2 times as strong as in the case of Plate III., no variation in the relative intensity of the diagram-lines and

the satellites was observed *. It is very difficult to draw any definite conclusion from a comparison of Plate I. on the one side and Plates II., III. on the other side, as these plates have been taken with different tensions. But at any rate it is very remarkable that no appreciable difference between these plates could be observed. A great difference, however, was observed between Plate IV. and the other plates.

On this plate only one line could be observed on the short wave-length side of α_1. This line was extremely faint, and seemed to have about the same wave-length as α_3. As the diagram-lines on this plate seemed not to be quite as strong as on the other plates, a fifth plate was taken under the same conditions as Plate I., but with a time of exposure of $1\frac{1}{2}$ minute. On this plate the lines α_1 and α_2 were certainly not stronger than on Plate IV., whereas the satellites could very well be seen.

The great difference between Plate IV. and the other plates is easily explained if we assume that by an impact with one single β-particle more than one electron at the same time may be removed from the atom. The energy connected with the removing of an electron from the L_1-level corresponds for Ag to 3350 volts. Thus, if two electrons should be removed at the same time from the L-shell, the tension on the tube must be at least more than 6700 volts. It is hardly probable that the maximum tension on the tube should have this value in the case of Plate IV.; therefore the lines corresponding to a double ionization of the L-shell could not appear on this plate. The one satellite which still was present on Plate IV. may be due to atoms which have lost at the same time one electron from the L-shell and one electron from the M-shell.

Further, these experiments indicate that it should be possible not only to obtain information about the state of the atom in which a certain satellite is emitted, but also to gain more insight into the laws governing the disturbance of an atom by an impact with a β-particle. This was shown by some photographs taken of the β_2 satellites (β_{11} and β_{12}) of silver with different tensions. These lines are very broad and diffuse. Under conditions differing about the same as those of Plates I. and III. in the above table, no change in

* From a comparison of Plates II. and III. it appears that the intensity of the spectral lines is not proportional to the current through the tube. There is no real difficulty in this, as we have to expect that the intensity of the spectral lines is proportional to the current density in the focus-spot on the anticathode rather than to the total current.

the relative intensity of these lines in regard to the line β_2 was observed. Photographed with the higher tension, however, they seem to be much more intense on their long wave-length side than on the other side. This difference was not observed on the plates taken with the lower tension.

I intend to continue these researches, using a direct-current source of high tension.

§ 8. From these results and the considerations of the former paragraphs it is evident that we cannot agree with the theoretical interpretation given by Mr. Wentzel of the fine structure of the absorption discontinuities. It is well known that the researches by Fricke*, Stenström †, and Hertz ‡ showed that at a short distance from the principal discontinuity another discontinuity may be found. The photographs give the impression that there are two white lines; the most intense of which usually lies on the long wave-length side. From this we may conclude that two different, rather definite, frequencies are selectively absorbed. According to Wentzel, the principal discontinuity should be connected with the removal of the first electron from the corresponding shell to the outside of the atom, the second with the removal of the second electron. As it seems very improbable that this successive ionization really takes place, it seems to be more likely that this structure of the absorption-edge is connected with the conditions at the outer side of the atom, as has been suggested by Kossel §. In this connexion it may be pointed out that in this laboratory Mr. Lindh has found rather great differences for the wave-lengths of the principal discontinuities of the same element in different chemical compounds.

§ 9. For the elements Ti (22), V (23), and Cr (24) Fricke also found a second discontinuity lying on the *long* wave-length side of the principal discontinuity. It is very probable that this anomalous discontinuity, as already has been suggested by Wentzel, is connected with the completion of the inner M-shell, which, according to Bohr, takes place in the neighbourhood of the iron group. I shall give an explanation of the appearance of this anomalous discontinuity, which differs from that given by Wentzel in some essential details. Wentzel suggests that in the region of the iron group the M-shell may occur in different modifications in different atoms of the same element, and especially that there are

* Fricke, Phys. Rev. xvi. p. 202 (1920).
† Stenström, *Dissertation Lund*, 1919.
‡ Hertz, *Zeitschrift f. Physik*, iii. p. 19 (1920).
§ Kossel, *Verhandlungen d. D. Phys. Ges.* xviii. p. 339 (1916).

found some atoms for which the M-shell has one electron more than usual. The principal discontinuity should be connected with the removal of an electron from the K-shell of a "normal" atom, the anomalous discontinuity with the removal of an electron from the K-shell of an atom whose M-shell has one electron more than usual.

I. however, suggest the following explanation. We will assume that the atoms of the same element have all the same initial state. The removal of one electron from the K-shell by absorption of X-ray energy may, however, happen in different ways. The electron may be removed wholly to the outside of the atom, a process which should correspond to the principal discontinuity, or the electron may be removed from the K- and enter the M-shell, which for the elements in question is in a state of development*. The latter process should correspond to an anomalous absorption-line lying on the long wave-length side of the normal absorption-edge. Besides, we may assume that, if in the latter case the regeneration of the K-shell takes place by an electron of the M-shell, this should give rise to a line which should have *exactly* the same wave-length as the corresponding absorption-line. Such a line has actually been found by Hjalmar† (compare Part V. § 5). If this explanation is correct, we should have in this line an example of a line which appears at the same time as emission and as absorption-line. A line of this type is only possible in a region of the periodic system where the initial level corresponds to a shell which is in a state of formation.

Now we may assume that in the rare-earth group where the N-shell is in a state of formation we should have the same phenomena. For these elements an electron may be removed from the L-shell under two different conditions : it may be removed wholly to the outside of the atom, or it may be transferred from the L-shell to the N-shell. The first transition should correspond to the normal absorption-edge, the second to an absorption-line lying on the short wave-length side of the edge. Besides, the inverse process of the second transition should give rise to an emission-line lying on the long wave-length side of a diagram-line, and having exactly the same wave-length as the corresponding absorption-line.

Anomalous satellites lying on the long wave-length side of diagram-lines have actually been found in the emission

* Compare N. Bohr, *Zeitschr. f. Physik*, vi. p. 1 (1922). See especially p. 60, where the possibility of such a transition has been suggested.

† Hjalmar, Phil. Mag. xli. p. 675 (1921). Hjalmar calls this line $K\beta'$.

spectrum of the rare-earth metals (compare Part IV. § 11 and Part V. § 5). If these lines may be explained in the above way, we must expect that they also appear as absorption-lines. In this case, however, we should have the remarkable fact that the difference between these absorption-lines and the corresponding normal absorption-edges should be quite considerable (*i. e.*, in the case of L_1 for Tb about 40 X.U. corresponding to 250 volts). I intend to start an experimental investigation about this matter.

Summary.

This paper has been divided into 5 Parts : Parts I., II., and III. have already been published in Phil. Mag. xliii. p. 1070 (1922).

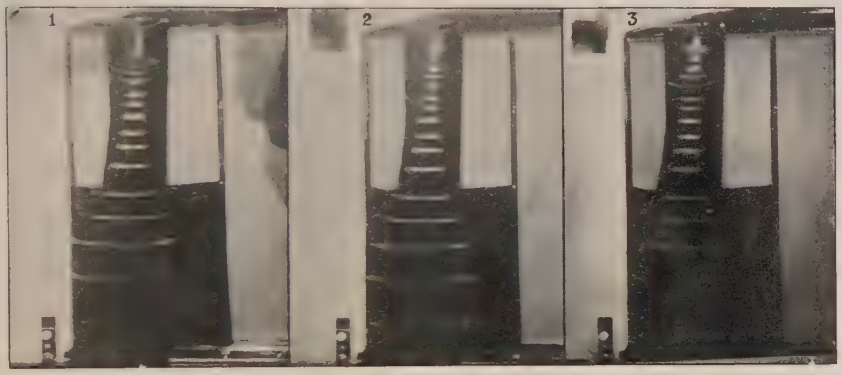
In Part I. the general laws governing the emission of the characteristic X-ray spectrum have been dealt with and the relation between these laws and Bohr's theory of atomic structure has been discussed.

Parts II. and IV. contain the new experimental results, Part II. gives the new measurements in the L-series of the elements Rb–Ba, Part IV. those of the elements La–Lu. These measurements comprise : 1°, a great number of lines which may be arranged in a simple diagram, these are denoted as diagram lines; 2°, some non-diagram lines ; 3°, some absorption discontinuities.

Parts III. and V. give a theoretical discussion of the new measurements. From this discussion it appears that the new results as regards the diagram lines are in beautiful agreement with Bohr's theory as regards the successive development of the shells of electrons in the atom (Part III. §§ 1–7).

According to Bohr, at different stages of the periodic table we meet with atoms for which an inner shell of electrons is completed. Thus the M-shell is completed in the neighbourhood of the iron group, the inner N-shell is partly completed in the region of the Pd group and again definitely for the rare-earth metals. The appearance of the Pt metals is connected with the partial completion of the inner O-shell. This conception is found to be in agreement with the experimental results. Especially for the completion of the N-shell in the region of the rare-earth metals several experimental proofs have been given (Part III. § 8).

Again, according to Bohr, we must expect that, where an inner shell is being completed, the most loosely bound electrons of this shell are bound not more firmly than the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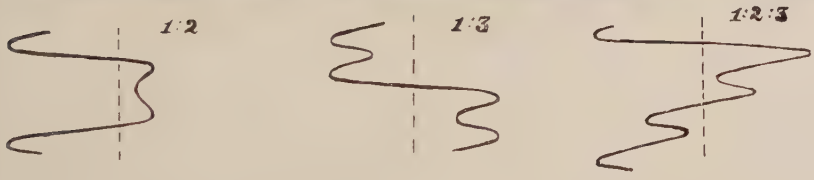
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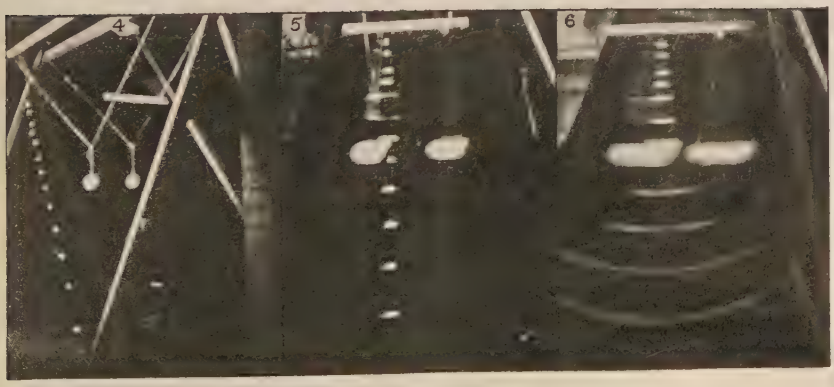
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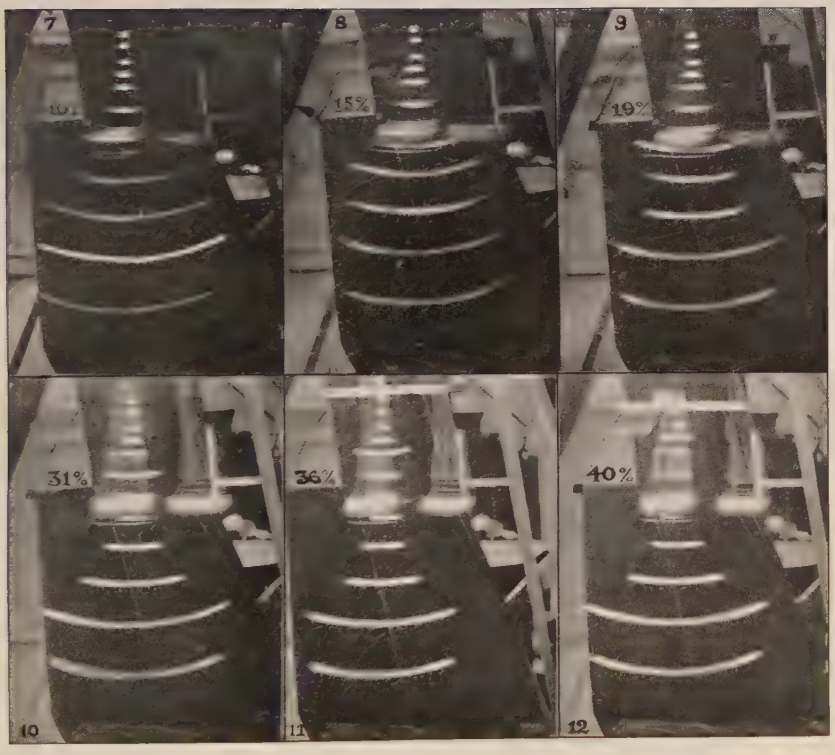

7
15%
8
15%
9
19%
31%
10
36%
11
40%
12

valency electrons belonging to the outermost shell. From the experimental data of this paper it could be proved that this is really the case (Part V. §§ 2 and 3).

In Part V. §§ 6–9 a theoretical discussion has been given of the non-diagram lines and of the fine structure of the absorption discontinuities. An experimental proof has been given that part of the non-diagram lines are emitted by atoms which have lost more than one electron at the same time by an impact with one single high-speed β-particle (Part V. § 7). Furthermore, an explanation has been given of some non-diagram lines which lie at the long wave-length side of diagram lines, and it has been suggested that these lines should appear at the same time in the emission and in the absorption spectrum (Part V. § 9).

I am much indebted to the kindness and interest of Prof. M. Siegbahn and Prof. N. Bohr.

LI. *Vibrational Responders under Compound Forcing.* *By* Prof. E. H. Barton, *F.R.S.*, *and* H. M. Browning, *Ph.D.* *

[Plates III. & IV.]

IN previous papers †, experiments were described in which sets of responders were under double forcing, but these forces were quite independent of each other. The present paper deals with cases in which the vibrational responders in use are under forcing, either (1) from the compound harmonic motion of a single-pendulum driver, or (2) from the associated motions of two coupled pendulums.

In the first case they illustrate the analysis of a musical tone by the mechanism of the ear on the resonance theory of audition. In the second case they show the double resonance sometimes observed when dealing with two electrical circuits closely coupled, or two communicating resonating chambers used with thermophones.

Compound Harmonic Vibration.—To illustrate by a set of responders the analysis of a compound harmonic vibration, the apparatus was arranged as shown in fig. 1. A stout cord ACB is fixed at A and B and set in motion by the swinging of the pendulum CD. The mass of the bob D is made paramount, in order that it may be used as the driver ‡.

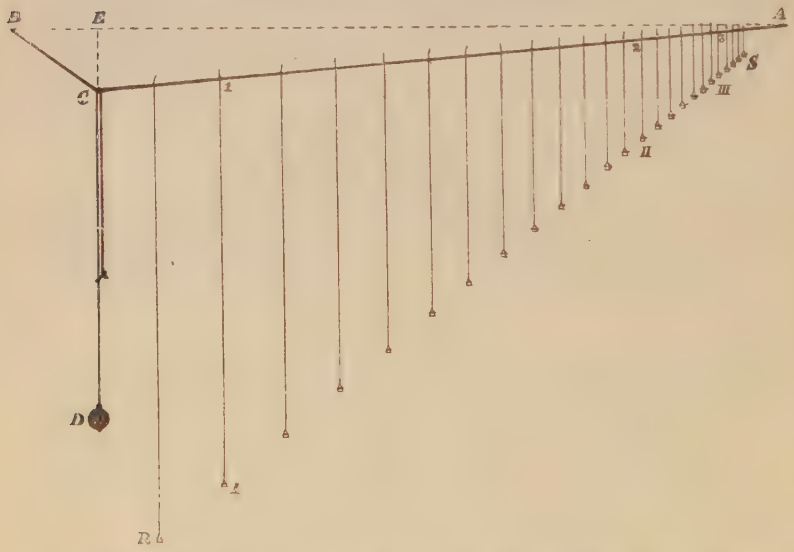
* Communicated by the Authors.

† Phil. Mag. vol. xxxvii. pp. 453-455, April 1919, and vol. xxxviii. pp. 163–173, July 1919.

‡ From this it follows that ABCD keeps the shape shown during vibration of D; hence the virtual length of this driving pendulum is ED.

The lengths of the twenty-five responders (R I....I I...I I I..S) range from one to sixteen, and are in geometrical progression. The distances from A of their suspension points are proportional to their lengths, so as to ensure that each shall receive an equal forcing from the driver. The advantage of this geometrical progression of length lies in the fact that the "intervals" (to use the musical expression) between adjacent responders are then all equal. Indeed, the whole set of twenty-five responders forms two octaves of the

Fig. 1.—Apparatus for Harmonic Analysis.



chromatic scale. It is to be noticed that these light vibrational responders have virtual lengths from their bobs to the cord AC and not to AEB. Their bobs consist of paper cones, with the addition of a ring of copper to diminish the damping to a suitable extent, and so make the resonance or response just sharp enough. The bobs were made precisely alike, and this ensured the damping being the same for each responder.

When first the bob D was allowed to swing freely, only one resonance maximum occurred in the vibration of the responders at the part marked I I in the diagram, thus showing that the motion was simple harmonic of the frequency thus indicated.

Next, the bob D was moved by hand in a compound harmonic motion of the same fundamental frequency as was natural to it. Then the responders showed the fundamental

frequency as before, but showed also by higher maxima the quicker vibrations which are the harmonic components of the compound motions now executed by D. Three cases of such harmonic analysis were carried out with this apparatus and the vibrations and results are shown in figs. 1, 2, and 3 of Pl. III. The curves shown below each indicate the motions given to the bob by hand, and the photographic reproductions above give time-exposures of the responders. In fig. 1 (Pl. III.) the motion is compounded of vibrations of relative frequencies one and two, or tone and octave, to adopt musical language. In fig. 2 the motion of the bob was compounded of vibrations of frequencies one and three, and the result of analysis is seen to be that of a tone and its twelfth. In fig. 3 the motion of the bob, as shown below, is compounded of frequencies one, two, and three, and the responders give maxima at the corresponding places, which the musician would call tone, octave, and twelfth.

Coupled Vibrations.—The arrangement now adopted is shown by the reproduction in fig. 4, Pl. III. There it may be seen that the two pendulums of nearly equal mass (each suspended by a bridle and vertical cord) are coupled by the bridge across the near part of the bridle. On the far part of the bridle of one pendulum a set of thirteen responders are in use. These are of precisely the same type and arrangement as the twenty-five used for the harmonic vibrations, but here only one octave of the chromatic scale is provided instead of two octaves. (The white cones which constitute the bobs are clearly visible, but the black suspension threads do not show.) For convenience, the responders may be named according to the chromatic scale of C. It was recently found to be far more convenient to have the bridge adjustable along the bridle instead of fixed at the junction of the bridle and vertical suspension for the heavy bob. If a line is drawn from the bridge across either of the coupled pendulums with heavy bobs to the distant end of the bridle, and the suspension cord imagined to stretch vertically upwards to meet this line, then the completed length of the suspension gives the vibrating length of the coupled pendulum when the bridge is held at rest, and therefore this length defines the quick period peculiar to the coupled system with the coupling in question.

Fig. 5 shows the effect of starting the vibration by burning a thread which held the bobs near together. In this case the bridge (as shown in the photograph) remains at rest, and the bobs execute the quick vibration alone. This is exhibited by the responders, which show a maximum amplitude at a

frequency between those of the fifth and sixth responders counting from the shortest (or in musical terms between A♭ and G).

In fig. 6, on the contrary, the effect is due to starting the pendulums simultaneously and in the same phase, so that each swings with bridle and suspension remaining in a plane. This isolates the slow motion of which the coupled pendulums are capable, and the responders now show a maximum amplitude at a frequency between D and D♭, to use the musical terms. The longest responder, C, does not show in the photograph.

In Pl. IV. are seen the effects of starting one pendulum while the other hangs free. This results in the quick and slow vibrations being performed simultaneously by each pendulum. Fig. 7 begins with about 10 per cent. coupling. This leads to the execution of frequencies so near alike that it is difficult to discriminate between them in the photograph. The response is here seen to be spread upwards as compared with fig. 6. In actually watching the responders, the beats between the two rates of forcing were clearly visible.

For a coupling of fifteen per cent., as shown in fig. 8, two maxima are distinctly visible. Musically speaking, the notes D and E are responding best, and the interval between them is one tone.

In passing from fig. 8 to 9, fig. 10 to 11, and fig. 11 to 12, the position of the upper maxima rises by one responder at a time, and it may be said musically that the pitch is raised by a semitone each time.

Between figs. 9 and 10 the pitch rises by a tone. Thus in fig. 12 the responders called D and A will be found to be the maxima, and the musical interval to be a perfect fifth. The couplings required for the various responses are shown on the Plate for each figure.

In order to show that the responders are responding accurately to the two vibrations of the coupled pendulums, traces might be taken on a board moving perpendicularly to the pendulums. But as this has been done for the pendulums alone, comparisons can be made between the figures on Pl. IV. of the present paper and Plate V. of "Vibrations under Variable Couplings," Phil. Mag. vol. xxxiv. Oct. 1917. It will be seen that fig. 12 of the present paper and fig. 7. of the Oct. 1917 paper have the same coupling, and that the ratio of the frequencies of the two component vibrations is approximately 3 : 2 in each case, though exhibited in entirely different ways.

Nottingham,
May 31, 1922.

LII. *The Measurement of Light.*

By Norman Campbell, *Sc.D., and* Bernard P. Dudding *.

Summary.

It is maintained that in order to establish a scientifically or legally satisfactory system of measuring any physical magnitude it is not sufficient to define the units to be employed: it is necessary also to state the laws of measurement involved. Photometry provides an exceptionally favourable illustration of this necessity; the laws of measurement underlying photometry are therefore considered in some detail.

1. International congresses have from time to time fixed with great elaboration the units of certain practically important physical magnitudes. The results of their labours are embodied, not only in scientific treatises, but also in much national legislation. It appears to be thought widely that, when the units have been fixed, an entire system of measurement has been established and that no further question can arise concerning the value to be attributed to any magnitude. We are of the contrary opinion. It appears to us, for example, that when the unit of resistance is fixed, we know certainly that one definite body has a resistance of 1 ohm; but we do not know certainly what other bodies have a resistance of 1 ohm or what bodies, if any, have a resistance of 2 ohms. And knowledge on these matters, which are not decided, is of much greater importance from every point of view than knowledge of those which are decided.

Let us put the matter practically. An Act of Parliament has laid down what is one ampere and one volt, and decided that one watt-second is the energy required to maintain one ampere under a potential of one volt for one second. Well and good. But when we are presented with our electric-light bills, we are asked to pay for a good many kilowatt-hours. And the Act has never told us what kind of current, under what kind of potential, for what kind of time, is the precise number of kilowatt-hours for which we are asked to pay. It appears to us that the Courts ought to decide that we cannot be legally forced to pay for anything but one watt-second, because otherwise we are paying for something of which the nature is wholly unknown to the law.

Doubtless counsel would advise us that, if we tried to

* Communicated by the Authors.

maintain such a position, the judicial mind might suffer one of its occasional lapses into common-sense. But while we would accept his view of the probable results of the action, we would protest that common-sense has nothing to do with the matter. It is not common-sense that tells us how to measure watts; it is the wisdom of the giants of physical science accumulated for more than a century. If we know quite definitely how to measure watts, we know all the fundamentals of electrical engineering and much of experimental physics. All measurement depends upon laws, and these laws usually include most of the important experimental facts of the science concerned with the magnitudes in question. Knowledge of these laws is not common property, and can no more be assumed than a knowledge of the customary units.

In opposition to our contention that a statement of the laws of measurement should be included with a description of the units in any defining legislation (by which we refer now to the decisions of scientific committees rather than to those of national legislatures), two arguments may be used. First, it may be said that the choice of units, being arbitrary, is suitable for legal decision, while the truth of laws, being wholly free from arbitrariness, is not; the first, therefore, but not the second, is suitable for inclusion in legislation. But surely, even in legislation, relevance is of some importance. Our only objection to present legislation on such matters is that it is totally irrelevant to all cases of practical importance; all that we suggest is that something should be added which will make it relevant. Secondly, it might be said that to meet our suggestion would be to convert the legislation into a complete treatise on science. But such a treatise would be either too large or too small for the purpose. It would be too small if we were urging that the impossible task should be performed of stating all the experimental laws that are concerned; it would be too large if we are urging (as we do) that the laws directly concerned should be indicated with a reasonable amount of precision. If we are asked what is meant by "directly" and "reasonable," we can only reply by giving an example. And that is what we propose to do.

2. Photometry seems a suitable system of measurement to choose: its measurements (even so far as units are concerned) have not yet been fixed completely with international consent; the laws of measurement concerned present some features of intrinsic interest; and some of the attempts at establishing systems of measurement that have been made

appear to us exceptionally unfortunate. Thus the inverse-square law, upon which most practical photometry depends, is treated very inadequately. The units cannot possibly be defined without reference to the law. It is usually implied, and not openly stated, as we hold it should be: and statement by implication is peculiarly objectionable here, because the law is only true in very special conditions which cannot be sufficiently described. But it is more serious that it is treated as a primary and necessary law for the measurement of all photometric magnitudes, so that the only form in which it can be stated with full precision is that photometric measurement is possible. This view seems to us utterly mistaken: one photometric magnitude at least can be defined without reference to it; and when that magnitude is defined the proposition can be stated as an independent law concerning it, and can be subjected to direct experimental proof. Closely connected with this defect is the total absence of any clear statement of the meaning of the addition of illumination, although in the practical use of light that law is much more important than the inverse-square law. It is more important to know that we can double generally the illumination by doubling the number of lamps than that we can multiply it four times by halving their distance. Lastly, the significance of the magnitudes is made to depend wholly upon a theory of illumination—the theory which may be baldly stated in the terms that illumination is due to the incidence of something called light. That theory is wholly unnecessary; and since, like all theories, it might be doubted, it should be studiously avoided and all definitions framed in terms of experimental concepts only.

With these preliminary remarks we will proceed to business. Perhaps the reader should be warned that what follows is not put forward as a model of an actual formulation, but merely as a sketch of the principles to be followed. The actual formulation would require much greater verbal precision and much less explanation of reasons for the scheme adopted.

The nomenclature of concepts concerned with measurement adopted here is that employed by one of us in 'Physics,' Part II.

3. Light-measurements are based on judgments of equality of brightness of photometric surfaces. These judgments are made by the direct perception of normal persons—normality in this matter meaning simply agreement with the great majority of mankind.

Photometric surfaces (P.S.) are members of pairs. A pair of photometric surfaces is defined by the condition that, if their positions are interchanged while everything else remains unaltered, equality of brightness is undisturbed whatever the nature of the illumination. P.S. which form a pair with the same P.S. form a pair with each other. The condition laid down ensures that the surfaces shall be of the same shape, including radius of curvature, of the same colour, of the same reflexion and diffusing coefficients, and of the same intrinsic luminosity. If it is fulfilled, it would be possible to use the pair of P.S. for light-measurement—unless, perhaps, if they were absolutely black—for all or for some colours. But it is convenient to choose surfaces which fulfil as nearly as possible other conditions which ensure that the surfaces are white, matt, and non-luminous. White is here used to include grey. A white surface is one such that light reflected from it is of the same colour as the direct light whatever the nature of that light; similarity of colour is judged by direct perception. A pair of matt surfaces are such that, if they are equally bright when viewed from one direction, they are equally bright if viewed from any other. No actual surfaces fulfil these conditions perfectly; none are perfectly white or perfectly matt. But some surfaces fulfil the condition very nearly, and these are best adopted for photometry. Further, it is desirable to choose surfaces which are white (in the ordinary sense) rather than grey; that is to say, if B, substituted for A, is less bright than A, A should be preferred to B. And, lastly, it is desirable to choose surfaces free from intrinsic luminosity, that is, such as can be made to appear perfectly dark by placing suitable screens round them.

4. The fundamental photometric magnitude is illumination. A pair of perfectly matt P.S. have equal illumination (or are equally illuminated) when they are equally bright. But since, as we have remarked, there are no perfectly matt surfaces, the law of equality, interpreted according to this definition, is not strictly true; the P.S. may be equally bright if viewed from one position, but unequally bright if viewed from another. If, however, a considerable change in the directions from which the surfaces are viewed does not change their relative brightness, the law of equality will be true for observations made within this range, and the definition so far will be satisfactory. The question remains, however, what is a considerable range for this purpose; it can only be answered perfectly definitely when the further definitions of measurement have been added; it can then be

stated that the range must be such that the entire system of measurement established is satisfactory. But meantime conditions can be prescribed more nearly in which the definition will be satisfactory even if the P.S. are not perfectly matt.

There are two such conditions to be fulfilled: (1) The lines joining the two P.S. to the observing eye must make equal angles with the normals to those surfaces. (2) The lines joining the illuminating source (or sources) to the P.S. must make equal angles with the normals to those surfaces and with the lines joining the surfaces to the eye. The assumption that these angles are unique implies that the surfaces and sources are "points." Again, it is impossible to prescribe exactly what are points, except by reference to the completed system of measurement that we are about to establish. But the proposition which is important for our purpose is that, if the dimensions of the surfaces and sources are made sufficiently small compared with the distance between them, the definition applied subject to the conditions just stated will prove satisfactory, even if actual surfaces, not perfectly matt, are employed as P.S. We can therefore give instructions whereby satisfactory measurements can be made: and when once such measurements have been made, the range of permissible variation of the conditions is determined by the agreement of other measurements with those made under these standard conditions. Difficulties such as these in describing the precise conditions for satisfactory measurement occur in all branches of physics; but they are probably more acute in photometry than in most other branches.

It will be observed that the absence of perfectly matt surfaces has forced us to introduce at this stage the ideas of "a source" and illumination by a source, which properly belong to a later stage. We may, therefore, describe them rather more closely. A surface is said to be illuminated by a source when its brightness can be changed by changing the physical condition of some body (*e.g.*, by changing the current through an incandescent lamp) or by interposing suitable media between that body and the surface. The body, the condition of which thus affects the brightness of the surface, is a source illuminating it.

We can now state the first of the important laws of illumination which are not necessary laws of measurement of that magnitude. If a pair of equally illuminated P.S. are replaced in position by another pair of P.S., the second pair will also be equally illuminated, even if a member of the

first pair does not form a photometric pair with a member of the second. Since any surface (except an absolutely black one) can be used as a P.S. with a suitable pair, this law naturally leads us to regard illumination as something characteristic, not of the surface illuminated, but of the circumstances in which it is placed. We find, further, that among the most important of these circumstances are the positions of the surfaces relative to the sources and the nature of these sources. It is these laws which give us the first clues to a theory of illumination; but such a theory, though it is a very useful guide in seeking a satisfactory system of measurement, is best excluded entirely from any description of it.

5. We must now define addition. The illumination on a surface X from the sources A and B is equal to the sum of the illumination of X from A and the illumination of X from B, if A and B, when they are illuminating the surface, are always in the same physical state and in the same position relative to the surface whether they are acting together or singly.

With this definition, the first law of addition is true: cutting off the illumination from a source always decreases brightness. But the second law is not true in all circumstances; it is not true, for example, when the Purkinje effect is apparent. For, if R_1 and R_2 are red sources, B_1 and B_2 blue sources, and if the illumination from R_1 is equal to that from B_1 and that from R_2 to that from B_2, the illumination from R_1 and R_2 will not be always equal to that from B_1 and B_2. On the other hand, if all the sources are of the same colour, the second law is true; and it is true apparently if the sources, though of different colour, give sufficiently great illumination and fulfil some other minor conditions. The Purkinje and allied effects are simply failures of the necessary laws of photometric measurement, and any complete statement concerning such measurement must include the proviso that the conditions are such that these effects do not enter and that the laws of measurement are true. It must be insisted that the only logical way to describe these effects is in terms of the failures of the laws of measurement which they involve; to describe them in terms of the measurements which they make impossible, though it may be convenient and conduce to brevity for general purposes, is utterly ludicrous if precision is important.

6. We have now defined completely the magnitude illumination, and can proceed to measure it and to state significantly and prove experimentally the following important

numerical law concerning it :—The illumination on a surface A from a source X is inversely proportional to the square of the distance of X from A, so long as (1) X and A are "points" : (2) the angles between the line XA and any lines characteristic of X and A remain the same ; (3) the medium between X and A (or rather the variable part of it) is perfectly uniform and transparent ; (4) that the bodies surrounding X and A are perfectly black. Of course, as usual, these four conditions are really in part definitions of points, perfectly transparent media and perfectly black bodies, the significant proposition being that there are conditions in which the numerical law is true and that they are indicated by the crude meaning attributed to the terms used.

Though the principles involved in the fundamental measurement of illumination by means of the definitions of equality and addition are the same as those involved in any other fundamental measurement, it may be well to describe in some detail one form of experiment by which the inverse-square law might be proved.

Two plane P.S. A and B are taken. A is viewed along its normal, and any sources X (all of which must be points) illuminating it are disposed in fixed positions on the surface of a circular cone of any apical angle with this normal as axis. B is viewed at any convenient angle, and the sources Y illuminating it are placed in any convenient positions with regard to it. Some one constant source Y_0 is chosen arbitrarily and placed arbitrarily in some constant position relative to B. The illumination of B by Y_0 is arbitrarily chosen as unit. We proceed, then, to find two sources, X_1 and X_1' such that either of them, acting alone, makes the illumination of A equal to that of B. Each of these sources then gives unit illumination on A. X_1 and X_1' are then made to illuminate A together; Y_0 is extinguished and some other source Y_2 is found which, placed in a certain position, makes the illumination of B equal to that of A. X_1 and X_1' are now extinguished, and a source X_2 found which, in some position on the cone, makes the illumination of A equal to that of B. The illumination of A by X_2 is then 2. And so on for the other positive integral values of the illumination of A. Experiment shows that it is impossible to find sources which give negative values for the illumination. But fractional illumination can be obtained. In order to make the members of the standard series of illumination the value of which is $1/n$, we have to find n sources placed on the cone such that any one of them illuminating A makes the illumination of A equal to that of B when illuminated by some

source (to be discovered by trial and error) while all n of them acting at the same time make the illumination of A equal to unit illumination. And so on for the values m/n, and the completion of the standard series.

We now illuminate B by some point source which can be moved along a straight line passing through B. When the distance of Y from B is r, we find what member of the standard series gives the same illumination on A as Y on B. We then multiply r^2 by the value assigned to this member, and find, after a large number of trials, that there is some value of this product such that we cannot find any law to predict whether any value of it resulting from single observation will be greater than or less than this value. We have then proved the numerical law.

7. This numerical law, like almost any other, enables us to define a derived magnitude, namely, the constant product Ir^2. Experiment shows that this constant is indeed a magnitude, an ordered property of the system under consideration, determined by and in general variable with (1) the nature of the point source, (2) the constant imperfectly transparent medium (if any) intervening between it and the P.S., (3) the direction of the line joining the source to the P.S. relative to lines characteristic of the source, (4) the angle θ which that line makes with the normal to the P.S. We shall suppose that (2) is not important because all the medium is perfectly transparent. Experiment shows that Ir^2 is approximately proportional to $\cos\theta$. We might therefore define a new derived magnitude $Ir^2\sec\theta$, which would depend only on the source and on the direction of the P.S. relative to it; we might term it the intensity of the light emitted by the source in the direction of the P.S. and denote it by Φ. But since the $\cos\theta$ law is not accurately true, Φ would not be truly a magnitude; it is better to define Φ as the value of Ir^2 when $\cos\theta=1$; it is then totally independent of the $\cos\theta$ law, and the limitation to one value of θ is not practically troublesome.

8. Φ is a function, not only of the nature of the source, but also of the direction of the P.S. relative to it. We can eliminate the direction and obtain a magnitude depending only on the nature of the source, if we can form the sum $\int\Phi d\omega$, where ω is the solid angle subtended at the source by the P.S. in any direction. The formation of this sum will be legitimate if the inverse-square law is obeyed whatever the direction, so that there is a Φ in every direction, and if Φ is independent of ω, the direction being the same: these

conditions are fulfilled if the P.S. and the source are sufficiently small. $\int \Phi d\omega$ when the sum is taken over all directions from the source is called the flux of light from the source ; if it is taken over a limited range of directions, it is called the flux emitted within the limit of those directions (F). The name that we (and everyone else) have chosen for this magnitude is, of course, suggested by a theory of illumination ; but it is essential to notice that it can be defined wholly independently of any theory. The magnitude is very important, because it is closely connected with the energy lost by the source and, through that energy, with the magnitudes of other branches of physics. Accordingly, it is often useful to invert the relations at which we have arrived and to express intensity and illumination in terms of flux. It is apparent that intensity is the flux per unit solid angle subtended by the P.S. at the source, and illumination the flux per unit area of the P.S. ; but it must always be remembered that these definitions are inverted and that really we know nothing about flux till we have measured illumination. Again, once we have arrived at the connexion between flux and illumination we may use this connexion to measure flux when the conditions which we have hitherto supposed necessary for its measurements are not fulfilled. Thus, even when a surface is illuminated by a source or sources which are not a single point obeying the inverse-square law, we may say that the flux incident upon it is the product of the illumination and the area. If we make this purely verbal definition of flux, we then find (in virtue of the law of addition of illumination) that the flux from many point-sources incident on a surface is the sum of that incident from each of them ; when we can use a definition to state a law, the definition ceases to be purely verbal and becomes an expression of fact : it may be admitted to our scheme on a parity with the other definitions of measurement.

9. One important photometric magnitude remains for discussion, brightness. We have used the conception of brightness before as something directly perceived, but we have not framed any scheme for measuring it. The magnitudes already established enable us to measure brightness as a derived magnitude. Let us take several surfaces which are unequally bright, though each of them is uniformly bright, and allow them in turn to illuminate a P.S., and measure the illumination of that P.S. (from which we deduce the intensity Φ of the light falling on it), the area S of the bright surface and the angle α which the line joining

the P.S. to the surface makes with its normal. Then we find as a matter of experimental fact that, when the inverse-square law is true, Φ is proportional to S; and that if we form the expression $\frac{\Phi}{S \cos \alpha}$, the order of this expression for the different sources is the order of their brightnesses directly perceived; the source for which the expression is the greater is always the brighter. That is equivalent to saying that this expression is a measure of the brightness: and accordingly we define the brightness of the surface, now a magnitude, as the intensity of the light emitted by it in a given direction divided by the area of the projection of the surface on a plane normal to the direction of viewing.

In general brightness so defined is a function of the angle α, in accordance with the fact that surfaces in general alter in brightness when the direction of viewing is changed. But there are certain surfaces, which are those most nearly matt, the brightness of which does not depend greatly on that angle. For such surfaces, the intensity of the light emitted at angle α is proportional to $\cos \alpha$; *i. e.*, Lambert's law is true. When Lambert's law is not true, if brightness is to be defined uniquely, some convention concerning the relevant values of α must be introduced. It is usual* to define brightness only for $\alpha = 0$; another course, in some ways more satisfactory, would be to take the mean brightness over the whole range of α.

So far we have regarded the measurement of the intensity of the light emitted by a known area of a bright surface as a mere means of measuring the brightness directly perceived. But for some purposes this intensity is important on its own account, *e. g.*, when we are considering the illumination that the bright surface would produce. For the purpose of this illumination it is immaterial whether the bright surface is or is not uniformly bright; so long as the intensity of the light emitted by unit area is the same, it does not matter whether the light comes from all parts of the surface or only from a few specks on it. Accordingly, it has become customary (though we think the custom unfortunate) to speak of all surfaces as equally bright so long as the intensity of the light from them per unit area (or possibly unit projected area) is the same, regardless of the fact that the apparent brightness of the surfaces, the quality directly perceived, is utterly different.

10. There remain to be considered certain subsidiary laws,

* *Cf.* Winkelman, *Handbuch der Physik, Optik*, p. 747 (2nd Ed.).

which, though not absolutely necessary to photometry, are useful in its more elaborate developments. It is doubtful whether they should be included in any official statement concerning photometric measurement: for it is difficult to describe precisely the circumstances in which they are accurately true, and in the last resort measurements should always be checked by the basic methods that have been described so far. But three of them may be noted. The first arises when reflecting or refracting surfaces are placed between the P.S. and the source or (more often) the eye. We have then to note that the line joining the P.S. to the source or eye is to be taken as the optical path between the two, and all statements concerning direction or distance interpreted accordingly. The second arises when a sphere-photometer is used to measure average flux or average candle-power. The law involved is then that the illumination of the P.S. used in the measurement is determined wholly by the average intensity of the source in the sphere. This proposition is never true universally, and only experiment with each photometer can tell within what limits it is true. The last is Talbot's law, employed in rotating sector methods or when asymmetrical sources are rotated to obtain average intensity. This law is apparently accurately true, and might therefore be included on an equality with the other laws of photometry.

11. Having stated the facts, we may proceed to conventions. We have to define the units of the various magnitudes. Since we have one fundamental magnitude (illumination) and three derived magnitudes (intensity, flux, brightness), we shall need n units arbitrarily assigned to some specified physical systems or substances and $4-n$ formal constants for the three numerical laws defining the derived magnitudes ($n<4$). We also need units of the other fundamental (or quasi-fundamental) magnitudes involved in the laws of derivation, namely, distance, solid angle, and surface. For many reasons it is convenient to make $n=1$. But it is important to observe that it is *not* necessary to assign to the arbitrarily selected system unit value of the fundamental magnitude; we can assign to it unit value of any of the connected magnitudes and define the unit value of the fundamental magnitude as if it were measured as quasi-derived.

This procedure is actually the most convenient; we assign arbitrarily a value of intensity and not of illumination. We describe a physical system which we call a standard candle. We then assert that the intensity of the light emitted by it

in some direction, specified by its relation to lines characteristic of that system, is 1. (*Intensity of standard candle*, or 1 *candle-power*.)

We choose the centimetre as unit of distance, square centimetre of area, and steradian of solid angle. We have now to choose the formal constants α, β, γ in the laws

$$\Phi = \alpha I r^2,$$

$$F = \beta \int \Phi d\omega,$$

$$B = \gamma \frac{\Phi}{S \cos \alpha}.$$

We have hitherto treated these constants as all being unity, but there is no reason, if we see fit, why we should not assign to them other values; and the choice of unity is as arbitrary as any other. As a matter of fact, α, β, γ are all usually chosen to be 1, and there is no objection to that practice. The unit of illumination (*phot*) is then that of a P.S. distant 1 cm. from the (point) standard candle in the prescribed direction; the unit of flux (*lumen*) that emitted by the standard candle within unit solid angle surrounding the prescribed direction, if the condition is fulfilled that the intensity is the same within all parts of that solid angle. The unit of brightness (*lambert*) is that of a perfectly matt surface which emits light of unit intensity when its area projected on the plane normal to the direction of viewing is one square centimetre. It is to be noted that these derived units (unlike the fundamental unit, which is not that of the fundamental magnitude) cannot all be actually realized. But such a feature of derived units is quite usual: *e.g.*, unit Young's modulus cannot be realized.

12. It may possibly be useful to compare our nomenclature and notation with that adopted by some official body. We choose for this purpose that of the Standards Committee of the Optical Society of America, described by its Chairman, P. R. Nutting *: —

Our Notation.		American.	
Illumination ...	I	Flux density ...	D
Intensity	Φ	Intensity	C
Flux	F	Flux	F
Brightness	B	Brightness	B

Of course, notation is a matter of mere convenience; but we have departed from the American scheme because we

* Journ. of the Opt. Soc. of America, iv. p. 230, July 1920.

think it is most highly inconvenient to denote the truly fundamental magnitude by a name (flux density) so highly suggestive of a derived magnitude. And we have preferred Φ to C in order to indicate the close connexion between intensity and flux.

But we have more serious differences with the American Committee. On p. 232 a lambert is defined as the brightness of a substance emitting one lumen per square centimetre of projected area in the direction considered. But to speak of a lumen emitted in *a* direction is to talk nonsense; the flux emitted within an infinitesimal angle is always infinitesimal. In place of "one lumen" should be substituted "one lumen per steradian." Since on p. 231 brightness is defined as flux per steradian per square centimetre, it is probable that the omission of the words "per steradian" is a mere oversight—the more unfortunate because it is twice repeated.

But the statement, also on p. 232, that "one candle per square centimetre equals 3·1416 lamberts" is less easily comprehensible. In the first place, lamberts have only been defined for surfaces which obey Lambert's law; for with other surfaces the lumens per steradian per unit of projected area will vary with the direction considered. Since a surface made up of "candles per square centimetre" does not obey that law, it is meaningless to attribute to it any number of lamberts. To remove this objection two alterations can be made:—(1) For "candles" can be substituted "candle-power"; for candle-power is often used as a synonym for what we and the American committee call intensity *. (2) Some specification can be added concerning the direction in which the candle-power or intensity is to be measured. For (2) it is most natural to take the direction normal to the surface; but if we take this direction, a surface of one square centimetre emitting an intensity of one candle-power (*i. e.*, one lumen per steradian) has a brightness of 1 lambert, not π lamberts as the American committee affirm. We might also take average intensity over a hemisphere based on the surface. If the surface is plane and obeys Lambert's law the average intensity over this hemisphere is $\frac{1}{2}$ candle-power per square centimetre, and a surface emitting 1 mean candle-power per square centimetre would be equal to

* *E. g.*, average candle-power or horizontal candle-power means average or horizontal intensity. The term "candles" is often here, too, used in place of candle-power. We believe that this confusion between a thing and its properties is one of the main sources of the obscurity of photometric definitions.

2 lamberts. Doubtless some function of the intensity and the angle could be devised such that, in a corresponding sense, one candle-power per square centimetre would be equal to π lamberts, but we cannot discover a function which has the least intrinsic plausibility. Doubtless the American committee have succeeded where we have failed, but they have been unduly modest in concealing their ingenuity ; they may fairly be asked to explain how they have arrived at their surprising result and why they have preferred it to the simple and obvious convention which gives the result that 1 candle-power per square centimetre equals 1 lambert.

May 27, 1922.

LIII. *Latent Heats of Vaporization and Expansion.* *By* D. L. Hammick*.

According to van der Waals, the pressure in a homogeneous fluid system is $p+\frac{a}{v^2}$. When the system expands, work is done against the pressure. The value of this work for the expansion of 1 gram of a liquid (volume v_1 c.c.) until its volume is v^2 c.c., the specific volume of the liquid when completely vaporized, is given by

$$\begin{aligned} A &= \int_{v_1}^{v_2}\left(p+\frac{a}{v^2}\right)dv \\ &= \int_{v_1}^{v_2} p\,dv + \int_{v_1}^{v_2}\frac{a}{v^2}\,dv \\ &= pv_1 - pv_2 - \frac{a}{v_1} + \frac{a}{v_2}. \end{aligned}$$

When v_2 is large when compared with v_1, this expression becomes

$$A = -pv_2 - \frac{a}{v_1},$$

or, putting pv_2 equal approximately to $\frac{RT}{M}$,

$$A = -\frac{RT}{M} - \frac{a}{v_1}. \quad \ldots\ldots\ldots \quad (1)$$

* Communicated by the Author.

From (1) we have, at constant volume,

$$T\left(\frac{dA}{dT}\right)_v = -\frac{RT}{M} - \frac{1}{v_1}\cdot\frac{da}{dT}\cdot T$$

$$= -\frac{RT}{M} - \frac{a}{v_1}\bar{a}T$$

$$\left(\bar{a} = \frac{1}{a}\frac{da}{dT}\right).$$

Hence, substituting in the equation

$$A - U = T\left(\frac{dA}{dT}\right)_v,$$

$$-U = -A + T\frac{dA}{dT} = \frac{a}{v_1}(1 - \bar{a}T) \quad . \quad . \quad . \quad . \quad (2)$$

$= \lambda_{ex.}$, the latent heat of the expansion.

Now Davies (Phil. Mag. [6] xxiv. p. 421) has obtained the following expression for π, the initial pressure in a fluid:—

$$\pi = \frac{4R}{v_c}(2T_c - T)$$

(v_c and T_c are critical volume and temperature).

Hence $$\frac{1}{\pi}\left(\frac{d\pi}{dT}\right)_v = -\frac{1}{2T_c - T}.$$

Davies has also shown (Phil. Mag. [6] xxiii. p. 415) that $\frac{1}{2T_c - T} = \alpha$, the coefficient of cubical expansion, so that

$$\frac{1}{\pi}\left(\frac{d\pi}{dT}\right)_v = -\alpha. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

But, if $\pi = \frac{a}{v^2}$, we get from (3):

$$\frac{1}{a}\left(\frac{da}{dT}\right)_v = -\alpha.$$

Substituting in (2)

$$\lambda_{ex.} = \frac{a}{v}(1 + \alpha T). \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When $T = 0$, we find $\lambda_{ex.} = \frac{a}{v_0}$: in other words, at the absolute zero the expression becomes identical with Bakker's expression for the latent heat of vaporization.

The question now arises as to the connexion between the value for the latent heat of expansion as given by (4) and the latent heat of vaporization at ordinary temperatures. The two latent heats would be equal, provided that no change in the internal energy of the substance occurred during the transition, at constant volume, from the liquid to the vapour phase. In other words, the condition for equality is :

$$\int_0^T C_v dT - \int_0^T c_v dT = 0. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(C_v, c are the specific heats at constant volume respectively.)

If (5) does not hold, then the difference between the latent heat of vaporization and $\lambda_{ex.}$ of equation (4) will be

$$\int_0^T (C_v - c_v) dT = H.$$

Again, if during the passage from the liquid to the gaseous state a change in molecular aggregation occurs, a further quantity of heat, h, representing heat of association, must be taken into consideration. Hence we may put

$$\lambda_{vap.} = \lambda_{ex.} + H + h. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In the Table values of $\lambda_{ex.}$, calculated according to equation (4) at the boiling-point, are compared with the observed values of $\lambda_{vap.}$, the latent heat of vaporization. Values of "a" are given as atmospheres pressure $\div$ (volume of 1 gramme molecule of gas at N.T.P.)^2 (Guye and Frederich, *Arch. Sci. phys. et natur. Genève*, ix. p. 22, 1900). Specific volumes and α, the coefficients of expansion, are taken from Young (Sci. Proc. Roy. Dubl. Soc. xii. p. 414, 1910) and Tyrer (Trans. Chem. Soc. 1914, p. 2534). The latent heats of vaporization refer to 1 gramme of liquid, and are mainly Young's values (*loc. cit.*).

It will be seen from the Table that the values of $\lambda_{ex.}$ at the boiling-point agree very well with the values of the latent heat of vaporization. At the boiling-point, therefore, we have, in equation (6),

$$H + h = 0.$$

For "normal" or unassociated liquids $h = 0$, and hence

$$H = \int_0^T (C_v - c_v) dT = 0.$$

TABLE.

Substance.	$T_{b.p.}$ ° A.	a. ats. (22·4 litres)²	v. c.c. per gram.	$\frac{a}{v}$ cals. per gram.	a.	$1+aT$.	$\lambda_{ex.}$ calc. cals. per gr.	$\lambda_{vap.}$ observed. cals. per gr.
Hydrogen	20·3	·00042[2]	1·429[1]	89·47	$\cdot 0_2 1116$[1]	1·227	110	108·5–113·2[3]
Nitrogen	67	·00276[2]	1·230[4]	34·82	$\cdot 0_2 569$[4]	1·438	50·04	49·83
Oxygen	85	·00272	·857[4]	37·75	$\cdot 0_2 426$[4]	1·362	51·4	53·8
Argon	87	·00260	·712[4]	27·95	$\cdot 0_2 385$[4]	1·385	38·7	37·5[5]
Ammonia	238	$\cdot 0_2 798$[3]	1·476[6]	227·7	$\cdot 0_2 176$	1·419	323	321[7]
N_2O	253	·0750	1·00	47·15	$\cdot 0_2 186$	1·472	69·4	66·9
Ether	308	·03688	1·431	56·08	$\cdot 0_2 169$	1·52	85·2	84·0
Pentane	313	·03915	1·622	59·96	$\cdot 0_2 163$	1·511	90·6	84·3
Methyl formate	313	·02355	1·059	75·22	$\cdot 0_2 157$	1·491	112·1	110·6
CS_2	323	·02412	·822	61·8	$\cdot 0_2 126$	1·407	86·95	85·0
Ethyl formate	323	·03302	1·133	64·64	$\cdot 0_2 159$	1·513	97·8	97·9
Methyl acetate	333	·03316	1·136	61·88	$\cdot 0_2 158$	1·528	94·6	98·6
Ethyl acetate	343	·04383	1·20	57·39	$\cdot 0_2 152$	1·521	87·3	85·8
Methyl-hexane	343	·05383	1·633	54·12	$\cdot 0_2 159$	1·544	83·6	81·9[10]
Fluor-benzene	353	·04272	1·053	53·61	$\cdot 0_2 142$	1·503	80·6	80·1
Propyl formate	353	·04388	1·199	57·46	$\cdot 0_2 150$	1·530	87·9	87·5
Methyl propionate	353	·04330	1·189	57·17	$\cdot 0_2 166$	1·586	90·7	89·0[8]
CCl_4	353	·04148	·676	31·6	$\cdot 0_2 35$	1·470	46·7	46·0
Benzene	353	·03945 (M).	1·233	64·03	$\cdot 0_2 138$	1·487	95·2	95·4
Methyl heptane	373	·06876	1·633	51·26	$\cdot 0_2 156$	1·582	81·1	75·8
Propyl acetate	373	·05659	1·257	52·67	$\cdot 0_2 155$	1·578	83·1	80·5[9]
Ethyl propionate	373	·05582	1·258	51·9	$\cdot 0_2 159$	1·593	82·7	81·8[8]
Methyl butyrate	373	·05577	1·240	52·55	$\cdot 0_2 156$	1·581	83·1	79·7[8]
Methyl isobutyrate	363	·05339	1·239	50·3	$\cdot 0_2 155$	1·565	78·7	76·3
Toluene	383	·05240	1·283	58·75	$\cdot 0_2 125$	1·478	86·8	86·8[8]
$SnCl_4$	383	·05926	·5021	21·12	$\cdot 0_2 141$	1·542	32·6	31·6
Methyl-octane	393	·08351	1·621	48·2	$\cdot 0_2 154$	1·606	77·4	77·4
Chlor-benzene	404	·05580	·983	47·54	$\cdot 0_2 124$	1·506	71·6	74·2
Bromo-benzene	433	·05692	·769	36·5	$\cdot 0_2 113$	1·490	54·4	55·2
Iodo-benzene	453	·06592	·633	30·5	$\cdot 0_2 114$	1·516	46·3	46·7
Acetic acid	393	·03732	1·068	118·2	$\cdot 0_2 123$	1·484	176·0	94·4
Water	373	·0118	1·044	424·7	$\cdot 0_3 766$	1·286	546	539
Acetone	329	·02617	1·321	71·56	$\cdot 0_2 149$	1·492	106·8	125·3
Ethyl alcohol	353	·02512	1·360	106·3	$\cdot 0_2 125$	1·441	153	220·9
Methyl alcohol	333	·01959	1·324	176·0	$\cdot 0_2 121$	1·402	246·6	289·2

[1] Dewar.
[2] Kaye and Laby's Tables.
[3] Keesom and Onnes (1913).
[4] Baly and Donnan, Jour. Chem. Soc. lxxxi. p. 907 (1902).
[5] Eucken, *Ber. deut. phys. Gesellsch.* xviii. p. 4 (1916).
[6] Lunge.
[7] Estreicher.
[8] Marshal and Ramsay, Phil. Mag. (5) xli. p. 28 (1896).
[9] Brown, Jour. Chem. Soc. lxxxiii. p. 987 (1903), lxxxvii. p. 265 (1905).
[10] Tyrer.

At the end of the Table are given some results for liquids ordinarily regarded as associated. It will be noticed that in the case of water the value of $H+h$ is approximately zero: in other words, $h+H$ must be nearly equal but opposite in sign.

Agreement between the values of $\lambda_{ex.}$ and $\lambda_{vap.}$ is not found at temperatures other than the boiling-point. Thus for ether at 0° C., $\lambda_{ex.} = 85{\cdot}5$ cals.; $\lambda_{vap.} = 92{\cdot}5$ cals. And from equation (4) it is easy to show that the slope of the $\lambda_{ex.}$ curve is given by

$$\frac{1}{\lambda_{ex.}}\frac{d\lambda_{ex.}}{dT} = -\frac{\alpha^2 T}{1+dT}.$$

Now at the boiling-point, αT is approximately ·5 (*vide* Table above. Hence

$$\frac{1}{\lambda_{ex.}}\frac{d\lambda_{ex.}}{dT} = -{\cdot}33\alpha.$$

The average value of $\frac{1}{\lambda_v}\cdot\frac{d\lambda_{vap.}}{dT}$ in the neighbourhood of the boiling-point is $2\alpha - 3\alpha$.

The Dyson Perrins Laboratory, Oxford.
May 12th, 1922.

LIV. *On the Faraday-Tube Theory of Electro-Magnetism.* *By the late* William Gordon Brown*.

1. THE method of describing a field of force by means of lines or tubes of induction, which originated with Faraday, was given a quantitative form by Sir J. J. Thomson†, and further discussed by N. Campbell in his book 'Modern Electrical Theory.' Since Maxwell himself looked on his work as a mathematical theory of Faraday's lines of force, one is tempted to examine the original physical theory for hints

* Communicated by Dr. C. G. Knott, F.R.S., General Secretary, R.S.E. The young author had just finished his school life at George Watson's College, Edinburgh, when the outbreak of war in 1914 called him to the service of King and Country. He met his death in France on November 13, 1916, at the age of 21. The paper was put in final form about a year earlier when W. G. Brown, after serving in Gallipoli, was in hospital. A short sketch of his life and of his other mathematical notes will be found in the Proceedings of the Roy. Soc. Edin. vol. xlii. 1921.

† 'Recent Researches,' chap. i.; 'Electricity and Matter,' chap. i.

as to the modification of the Maxwellian theory to suit certain modern requirements.

What is attempted in the present paper is a reconstruction of the quantitative theory of Faraday tubes on a dynamical basis from the minimum of hypotheses : partly to enable the electromagnetic consequences of altering the Principle of Action to be estimated, and partly to suggest plausible directions for modification of the electromagnetic relations themselves. It will incidentally be shown that the stress which may be supposed to act in the electromagnetic field requires certain modifications if the theory of lines of force is adopted.

2. The first assumption required is as follows :—A tube of induction, or Faraday tube, may be defined as a continuous line having certain physical properties. Any tube may either be a closed curve, or its ends be connected to a positive and a negative electric particle respectively ; the positive direction will then be from the positive to the negative particle. It would be superfluous at present to specify any further properties of the electric particles.

The tubes at any point may be divided into sets distinguished by each set having a common direction and a common velocity of translation.

In what follows the vectorial notation of Heaviside is employed *, and electrical quantities are measured in rational units. Let the density of the tubes of the mth set and their direction, at any point, be represented by the magnitude and direction of the vector $\mathbf{d}_m$; then the number of tubes of that set passing through unit area normal to the unit vector $\mathbf{N}$ will be $\mathbf{N}\mathbf{d}_m$.

Let
$$\mathbf{D} = \Sigma \mathbf{d}_m, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the summation including all the sets present at the point ;

* [Heaviside's vector notation is a modification of Hamilton's quaternion notation, the main difference being that the quaternion product of two vectors $\mathbf{AB}$ is not used in Hamilton's sense but is used to mean the scalar of the complete product—that is, Heaviside's $\mathbf{AB}$ is equivalent to Hamilton's $-\mathrm{S}\mathbf{AB}$, and may be defined geometrically as equal to $\mathrm{AB}\cos\theta$, where A, B are the lengths of $\mathbf{A}$, $\mathbf{B}$, and θ the angle between them. As in other non-associative vector algebras, the square of a vector is equal to the square of its length; in quaternions $\mathbf{A}^2 = -\mathrm{A}^2$. The notation introduced by Gordon Brown in equations (9), (10), etc., has been suggested by others but generally discarded. Burali-Forti and Marcolongo, however, make it a feature of their system of vector analysis. As a notation it is misleading; as an operator it is inferior to the quaternion Δ.—C. G. K.]

then the total of all sets passing through the same unit area is

$$\Sigma \mathbf{N}\mathbf{d}_m = \mathbf{N}\mathbf{D},$$

where tubes passing through the area in the direction of $\mathbf{N}$ are reckoned positive, and the algebraic total is intended. Thus $\mathbf{D}$ represents vectorially the total flux of tubes; it is to be identified with the $\mathbf{D}$ of Heaviside, and, except for the question of units, with the (f, g, h) of Maxwell.

Let $\mathbf{q}_m$ be the (vector) velocity of the tubes of the mth set at the point in question, and let

$$\mathbf{H} = \Sigma \mathrm{V}\mathbf{q}_m \mathbf{d}_m, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The quantity thus defined will be shown to have the properties of the magnetic force.

This completes the geometrical and kinematic specification of the properties of the tubes. It is not difficult to see that if we define the charge of an electric particle as the number of tubes *leaving* it, in the sense that the direction of the tubes at a positive particle is outwards, then the density of electric charge will be given by

$$\rho = \mathrm{div}\, \mathbf{D}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If we take the curl of (2) and expand the right member fully, interpreting the terms kinematically, we obtain the equation

$$\begin{aligned} \mathrm{curl}\, \mathbf{H} &= \dot{\mathbf{D}} + \Sigma \mathbf{q}_m \,\mathrm{div}\, \mathbf{d}_m \\ &= \dot{\mathbf{D}} + \mathbf{u}\rho, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4) \end{aligned}$$

where $\dot{\mathbf{D}}$ is the time rate of change of $\mathbf{D}$ *at a fixed point*, and $\mathbf{u}$ is the mean velocity of translation of the electric particles calculated so as to make $\mathbf{u}\rho$ the convection current.

The second assumption made is dynamical. Let us write

$$\mathbf{E} = \frac{\mathbf{D}}{\mathrm{K}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\mathbf{B} = \mu \mathbf{H}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where μ and K are constants, and $\mathbf{E}$ and $\mathbf{B}$ are new vectors, the electric intensity and magnetic induction.

Then we assume that the volume densities of kinetic and potential energy are given by

$$\mathrm{U} = \tfrac{1}{2}\mathbf{E}\mathbf{D}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\mathrm{T} = \tfrac{1}{2}\mathbf{H}\mathbf{B}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The meaning attached to the above quantities is that if we write

$$\mathrm{L}=\iiint(\mathrm{T}-\mathrm{U})dv,$$

where the volume integral is extended throughout all space, then L may be used as the Lagrangian function in equations of motion of the usual form. For the sake of brevity, vectorial general coordinates will be employed. In order to preserve the form of the equation

$$\frac{d}{dt}\frac{\partial \mathrm{L}}{\partial \dot{q}}-\frac{\partial \mathrm{L}}{\partial q}=0,$$

it is sufficient to write, in the case of a vector coordinate $\mathbf{r}$ (equivalent to the three scalar coordinates x, y, z),

$$\left.\begin{aligned}\frac{\partial}{\partial \mathbf{r}}=\nabla&=i\frac{\partial}{\partial x}+j\frac{\partial}{\partial y}+k\frac{\partial}{\partial z}\\ \frac{\partial}{\partial \dot{\mathbf{r}}}&=i\frac{\partial}{\partial \dot{x}}+j\frac{\partial}{\partial \dot{y}}+k\frac{\partial}{\partial \dot{z}}\end{aligned}\right\}\quad\ldots\quad(9)$$

This notation in vectorial analysis is of course not generally applicable, but is convenient for the purposes of the present paper. The general results of differentiation which will be required are

$$\frac{\partial}{\partial \mathbf{s}}\,\mathbf{a}\mathbf{s}=\mathbf{a},\quad\ldots\quad(10)$$

$$\frac{\partial}{\partial \mathbf{s}}\,\mathbf{s}\psi\mathbf{s}=2\psi\mathbf{s},\quad\ldots\quad(11)$$

where $\mathbf{s}$ is any vector variable, $\mathbf{a}$ is a constant vector, and ψ is a constant self-conjugate linear and vector operator.

4. To define the general coordinates, let all tubes at a given moment be divided into small unit lengths; and let $\mathbf{r}$ be the vector from a fixed origin to the centre of one such unit segment, which forms part of a tube of the mth set, then the Lagrangian equation corresponding to $\mathbf{r}$ will be

$$\frac{d}{dt}\frac{\partial \mathrm{L}}{\partial \dot{\mathbf{r}}}-\frac{\partial \mathrm{L}}{\partial \mathbf{r}}=0.\quad\ldots\quad(12)$$

Now, when a unit length of a tube of the mth set is added to, or removed from, an element of volume, the increase or decrease of the whole Lagrangian function due to this

element will be

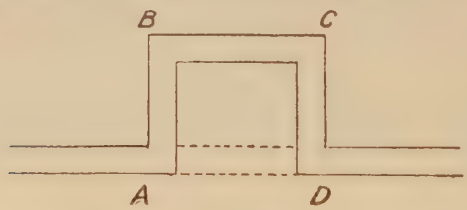
$$\delta L = \frac{\partial L}{\partial \mathbf{d}_m} \cdot \delta \mathbf{d}_m$$
$$= -\delta \mathbf{d}_m (\mathbf{E} + V\mathbf{q}_m \mathbf{B}), \quad . \quad . \quad . \quad (13)$$

for

$$\frac{\partial}{\partial \mathbf{d}_m} (T - U) = \frac{\partial}{\partial \mathbf{d}_m} \cdot \left[\tfrac{1}{2}\mu (\Sigma V\mathbf{q}_m \mathbf{d}_m)^2 - \tfrac{1}{2}\mathbf{D}^2/K \right]$$
$$= \frac{\partial}{\partial \mathbf{d}_m} \cdot \left[\Sigma\Sigma \tfrac{1}{2}\mu (-\mathbf{d}_m V\mathbf{q}_m V\mathbf{q}_s \mathbf{d}_s) - \tfrac{1}{2}(\Sigma \mathbf{d}_m)^2/(K) \right]$$
$$= -(\mathbf{E} + V\mathbf{q}_m \mathbf{B}), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where the summations include all values of the suffixes n, s, the differentiation of terms such as $(-\mathbf{d}_m V\mathbf{q}_m V\mathbf{q}_m \mathbf{d}_m)$ being performed by means of (11), since $(-V\mathbf{q}_m V\mathbf{q}_m)$ is a self-conjugate operator ; and that of cross-products, such as :—

$(-\mathbf{d}_m V\mathbf{q}_m V\mathbf{q}_s \mathbf{d}_s)$ by means of (10), writing $\mathbf{a} = -V\mathbf{q}_m V\mathbf{q}_s \mathbf{d}_s$.



Thus, if in the figure the unit segment is removed from the position AD (at which (14) has the value $-(\mathbf{E} + V\mathbf{q}_m \mathbf{B})$) to the parallel position BC (at which (14) has the value $-(1 + \delta r \nabla)(\mathbf{E} + V\mathbf{q}_m \mathbf{B})$, $AB = \delta r$), then the total increase in L is given by

$$\delta L = -\delta r \nabla \,.\, \delta \mathbf{d}_m (\mathbf{E} + V\mathbf{q}_m \mathbf{B}).$$

It will now be convenient to suppose (as we may without loss of generality) that the mth set consists of but one tube, so that $\delta \mathbf{d}_m = \mathbf{d}_m$ and is in fact a unit vector.

Then

$$\delta_1 L = -\delta r \nabla \,.\, \mathbf{d}_m (\mathbf{E} + V\mathbf{q}_m \mathbf{B}), \quad . \quad . \quad . \quad (15)$$

and in applying the axial differentiator $\delta r \nabla$ we must remember that neither $\mathbf{d}_m$ nor $\mathbf{q}_m$ as they occur explicitly are to be considered variable.

But to preserve the continuity of the tube we require to introduce the segments AB, CD, as shown in the figure, so

that, again applying (13), we have the change of L due to this cause

$$\delta_2 \mathrm{L} = \mathbf{d}_m \nabla \,.\, \delta \mathbf{r} (\mathbf{E} + \mathrm{V} \mathbf{q}_m \mathbf{B}), \quad . \quad . \quad . \quad . \quad (16)$$

in which $\mathbf{q}_m$ is variable (but not $\mathbf{d}_m$).

Hence

$$\delta \mathrm{L} = \delta_1 \mathrm{L} + \delta_2 \mathrm{L} = \delta \mathbf{r} [\mathbf{d}_m \nabla \,.\, (\mathbf{E} + \mathrm{V} \mathbf{q}_m \mathbf{B}) - \nabla \,.\, \mathbf{d}_m (\mathbf{E} + \mathrm{V} \mathbf{q}_m \mathbf{B})],$$

$\mathbf{q}_m$ varying in the first term only, and $\mathbf{d}_m$ not at all, and finally

$$\frac{\partial \mathrm{L}}{\partial \mathbf{r}} = \mathbf{d}_m \nabla \,.\, (\mathbf{E} + \mathrm{V} \mathbf{q}_m \mathbf{B}) - \nabla \,.\, \mathbf{d}_m (\mathbf{E} + \mathrm{V} \mathbf{q}_m \mathbf{B}) \quad . \quad (17)$$

with the same convention.

In calculating the momentum term $\dfrac{\partial \mathrm{L}}{\partial \dot{\mathbf{r}}}$ we have $\dot{\mathbf{r}} = \mathbf{q}_m$. Then by the method employed above in calculating (14), since T is symmetrical in $\mathbf{q}_m$ and $\mathbf{d}_m$,

$$\frac{\partial \mathrm{T}}{\partial \mathbf{q}_m} = \mathrm{V} \mathbf{d}_m \mathbf{B}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

This will be the value of $\dfrac{\partial \mathrm{L}}{\partial \dot{\mathbf{r}}}$ when $\mathbf{d}_m$ is a unit length of tube, but in performing the complete differentiation to time in (7) we must remember that any length of tube will in general be continually varying in direction and magnitude. It is clear that

$$\frac{d}{dt} \mathbf{d}_m = \mathbf{d}_m \nabla \,.\, \mathbf{q}_m, \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

since the rate of change of a segment of a straight line, as AD in the figure, will be the relative velocity of its ends (vectorially); while, of course, if $\mathbf{q}_m$ expresses the velocity of any point of the tube, as A, the velocity at D will be $(1 + \mathrm{AD} \nabla \,.\,) \mathbf{q}_m$, where $\overline{\mathrm{AD}}$ is the vector element.

Thus

$$\frac{d}{dt} \frac{\partial \mathrm{L}}{\partial \dot{\mathbf{r}}} = \frac{d}{dt} \mathrm{V} \mathbf{d}_m \mathbf{B}$$

$$= \mathrm{V} (\mathbf{d}_m \nabla \,.\, \mathbf{q}_m) \mathbf{B} + \mathrm{V} \mathbf{d}_m \dot{\mathbf{B}} + \mathrm{V} \mathbf{d}_m (\mathbf{q}_m \nabla \,.\, \mathbf{B}), \quad . \quad . \quad (20)$$

where $\dot{\mathbf{B}}$ is the rate of change of $\mathbf{B}$ at a fixed point coincident with the moving centre of the segment, $\mathbf{q}_m \nabla \,.\, \mathbf{B}$ being of course the term in the rate of change due to motion of the segment with velocity $\mathbf{q}_m$.

Equation (12) is therefore by (17) and (20),

$$\begin{aligned}&\mathrm{V}(\mathbf{d}_m\nabla\,.\,\mathbf{q}_m)\mathbf{B}+\mathrm{V}\mathbf{d}_m\dot{\mathbf{B}}-\mathrm{V}\mathbf{d}_m(\mathbf{q}_m\nabla\,.\,\mathbf{B})\\&-\mathbf{d}_m\nabla\,.\,(\mathbf{E}+\mathrm{V}\mathbf{q}_m\mathbf{B})+\nabla\,.\,\mathbf{d}_m(\mathbf{E}+\mathrm{V}\mathbf{q}_m\mathbf{B})=0,\quad(21)\end{aligned}$$

$\mathbf{d}_m$ and $\mathbf{q}_m$ being constant in the last term, and ∇ operating forwards only.

In carrying out the simplifying transformations we may drop for the moment the suffix m.

From the last two terms we have, in part,

$$\begin{aligned}-\mathbf{d}\nabla\,.\,\mathbf{E}+\nabla\,.\,\mathbf{d}\mathbf{E}&=+\mathrm{V}\mathbf{d}\mathrm{V}\nabla\mathbf{E}\\&=+\mathrm{V}\mathbf{d}\,\mathrm{curl}\,\mathbf{E}.\quad(22)\end{aligned}$$

From the remainder we find

$$\begin{aligned}&\mathrm{V}\mathbf{d}\dot{\mathbf{B}}+\mathrm{V}(\mathbf{d}\nabla\,.\,\mathbf{q})\mathbf{B}+\mathrm{V}\mathbf{d}(\mathbf{q}\nabla\,.\,\mathbf{B})-\mathbf{d}\nabla\,.\,\mathrm{V}\mathbf{q}\mathbf{B}+\nabla_1\,.\,\mathbf{d}\mathrm{V}\mathbf{q}\mathbf{B}_1\\&=\mathrm{V}\mathbf{d}\dot{\mathbf{B}}+\mathrm{V}(\mathbf{d}\nabla\,.\,\mathbf{q})\mathbf{B}+\mathrm{V}\,.\,\mathbf{d}(\mathbf{q}\nabla\,.\,\mathbf{B})\\&\quad-\mathrm{V}(\mathbf{d}\nabla\,.\,\mathbf{q})\dot{\mathbf{B}}-\mathrm{V}\,.\,\mathbf{q}(\mathbf{d}\nabla\,.\,\mathbf{B})+\nabla_1\,.\,\mathbf{d}\mathrm{V}\mathbf{q}\mathbf{B}_1\\&=\mathrm{V}\mathbf{d}\dot{\mathbf{B}}+\mathrm{V}\,.\,\mathbf{d}(\mathbf{q}\nabla\,.\,\mathbf{B})-\mathrm{V}\,.\,\mathbf{q}(\mathbf{d}\nabla\,.\,\mathbf{B})\\&\quad-\mathrm{V}\,.\,\mathbf{d}(\mathbf{q}\nabla\,.\,\mathbf{B})+\mathrm{V}\,.\,\mathbf{q}(\mathbf{d}\nabla\,.\,\mathbf{B})+\mathrm{V}\mathbf{d}\mathbf{q}\,.\,\nabla\mathbf{B}\\&=\mathrm{V}\mathbf{d}\dot{\mathbf{B}}+\mathrm{V}\mathbf{d}\mathbf{q}\,\mathrm{div}\,\mathbf{B},\quad(23)\end{aligned}$$

where the suffix restricts the action of ∇ to the vector carrying the same suffix.

Equation (21) then reduces to

$$\mathrm{V}\mathbf{d}_m(\mathrm{curl}\,\mathbf{E}+\dot{\mathbf{B}}+\mathrm{div}\,\mathbf{B}).\quad(24)$$

Now $\mathbf{d}_m$ will have different values according to the different directions of the various sets of tubes; hence (unless all the tubes are parallel) we may write

$$\mathrm{curl}\,\mathbf{E}+\dot{\mathbf{B}}+\mathbf{q}_m\,\mathrm{div}\,\mathbf{B}=0.\quad(25)$$

From this, since $\mathbf{q}_m$ is the velocity of any set of tubes, unless all the sets have a common velocity, we must have

$$\mathrm{div}\,\mathbf{B}=0,\quad(26)$$

and thus

$$-\mathrm{curl}\,\mathbf{E}=\dot{\mathbf{B}}.\quad(27)$$

We have now shown that the first four laws of the ordinary theory of electromagnetism are consequences of the assumptions which have been made. It may be observed that whereas, in the proof of the first two laws (3) and (4), no departure of importance is made from the method of 'Recent Researches,' the proof just given of the laws (26) and (27) is quite different from that adopted in that work. This is

rendered necessary by the purpose of the present paper, which is not to deduce the properties of the tubes from the known laws of electromagnetism, but to show that, given the tubes with the (essential) properties assigned to them by Sir J. J. Thomson, the laws of electromagnetism follow.

5. It remains to discuss the forces acting on the electric particles. Referring to the figure on p. 598, let B be a particle at the end of the tube B, C, D. Then the change in L due to the displacement of the end of the tube from B to A (introducing a new segment BA), is by (13)

$$\delta \mathrm{L} = \delta \mathrm{r}(\mathbf{E} + \mathrm{V}\mathrm{q}_m\mathbf{B}), \quad . \quad . \quad . \quad . \quad . \quad (28)$$

since

$$\delta \mathrm{d}_m = \overline{\mathrm{AB}} = -\delta \mathrm{r},$$

B being the positive end of the tube, and thus equivalent to a positive unit of electricity. Hence the force acting per unit charge moving with velocity q is

$$\mathbf{F} = \mathbf{E} + \mathrm{V}\mathrm{q}\mathbf{B}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

the Fifth Law of Electromagnetism.

6. The definite dynamical assumptions of this theory enable us to examine very thoroughly such questions as the stress in the field and the mechanism of radiation.

Heaviside * has given a general discussion of the problem of stresses from which it is not difficult to deduce the following general result :—

Let ψ_0 be the operator of Maxwell's stress,

$$\psi_0 = \mathbf{E} \,.\, \mathbf{D} + \mathbf{H} \,.\, \mathbf{B} - \tfrac{1}{2}(\mathbf{E}\mathbf{D} + \mathbf{H}\mathbf{B}), \quad . \quad . \quad . \quad (30)$$

where any vector operand forms with **D** and **B** scalar products in the first and second terms. When this operand is a unit vector **N**, $\psi_0\mathbf{N}$ is the stress on the plane perpendicular to **N**.

Let ψ be the stress derived from ψ_0 by putting for **E**, $\mathbf{E} + \mathrm{V}\mathrm{q}\mathbf{B}$, and for **H**, $\mathbf{H} - \mathrm{V}\mathrm{q}\mathbf{D}$, namely

$$\begin{aligned} \psi &= \psi_0 + \mathrm{V}\mathrm{q}\mathbf{B} \,.\, \mathbf{D} - \mathrm{V}\mathrm{q}\mathbf{D} \,.\, \mathbf{B} - \tfrac{1}{2}(\mathrm{V}\mathrm{q}\mathbf{B})\mathbf{D} + \tfrac{1}{2}(\mathrm{V}\mathrm{q}\mathbf{D})\mathbf{B} \\ &= \psi_0 + \mathrm{V}\mathrm{q}\mathbf{B} \,.\, \mathbf{D} + \mathrm{V}\mathbf{D}\mathrm{q} \,.\, \mathbf{B} - \mathbf{D}\mathrm{V}\mathrm{q}\mathbf{B} \\ &= \psi_0 + \mathrm{V}\mathbf{D}\mathbf{B} \,.\, \mathrm{q} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31) \end{aligned}$$

by mere vector transformation.

Then if **N** is unit normal to a surface moving with a velocity q at any point, $\psi\mathbf{N}$ is the flux of momentum through the surface in the direction opposite to the positive direction of **N**, per unit surface per unit time.

* 'Electrical Papers,' vol. ii. pp. 521 *et seq.*; also Phil. Trans. A. 1892

To see that this is true we have only to apply the theorem of divergence; in the first place we note that since

$$\frac{\partial \mathrm{T}}{\partial \mathrm{q}_m} = \mathrm{V}\mathrm{d}_m\mathbf{B}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

summing for all values of m we have $\mathrm{V}\mathbf{DB}$ equal to the momentum per unit volume. But

$$\psi_0\nabla = \frac{\partial}{\partial t}\mathrm{V}\mathbf{DB}, \quad . \quad . \quad . \quad . \quad . \quad (32)$$

a result easily deduced (Heaviside, *loc. cit.*) from the circuital laws, and usually expressed in words by stating that Maxwell's stress gives rise to a translational force per unit volume equal to the rate of change at a fixed point of the momentum per unit volume (the absence of electrification being assumed). We are thus entitled to say that $\psi_0\mathbf{N}$ is the flux of momentum per unit area of a fixed surface. Now it is clear that $\mathrm{V}\mathbf{DB}.\mathbf{qN}$ is the flux per unit area due to the motion of the surface with velocity $\mathbf{q}$. Hence ψ is the general operator giving the flux of momentum. The equation of rate of change of momentum per unit volume at a point whose velocity is $\mathbf{q}$ is

$$\begin{aligned}\psi\nabla &= \frac{\partial}{\partial t}\mathrm{V}\mathbf{DB} + \nabla\mathbf{q}\,.\,\mathrm{V}\mathbf{DB} \\ &= \frac{\partial}{\partial t}\mathrm{V}\mathbf{DB} + \mathbf{q}\nabla\,.\,\mathbf{DB} + \mathrm{V}\mathbf{DB}\,.\,\mathrm{div}\,\mathbf{q}, \quad . \quad . \quad (33)\end{aligned}$$

the first two terms giving the rate of change of density of momentum at the moving point, and the last term the rate of change due to expansion at the rate $\mathrm{div}\,\mathbf{q}$.

This flux of momentum ψ is partly due to convection, and partly to be ascribed to a stress. It is interesting to note that if all the tubes were of one set, we could determine the stress by simply putting $\mathbf{q}$ equal to this velocity. We should then have $\mathbf{H} = \mathrm{V}\mathbf{qD}$, and the stress would be

$$\begin{aligned}\phi &= (\mathbf{E} + \mathrm{V}\mathbf{qB})\,.\,\mathbf{D} - \tfrac{1}{2}(\mathbf{E} + \mathrm{V}\mathbf{qB})\mathbf{D} \\ &= \mathbf{F}\,.\,\mathbf{D} - \tfrac{1}{2}\mathbf{FD} \\ &= \mathbf{F}\,.\,\mathbf{D} + \tfrac{1}{2}(\mathbf{HB} - \mathbf{ED}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)\end{aligned}$$

In general the stress operator will be obtained by subtracting from ψ_0 the operator $-\Sigma(\mathrm{V}\mathrm{d}_m\mathbf{B}\,.\,\mathbf{q}_m)$ which gives the convective flux of momentum relative to a fixed point; thus

the stress is

$$\phi=\psi_0+\Sigma(\mathrm{V}\mathfrak{d}_m\mathbf{B}\,.\,\mathfrak{q}_m). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)'$$

$$=\mathbf{E}\,.\,\mathbf{D}+\mathbf{H}\,.\,\mathbf{B}-\tfrac{1}{2}\mathbf{E}\mathbf{D}-\tfrac{1}{2}\mathbf{H}\mathbf{B}+\Sigma\mathrm{V}\mathfrak{q}_m\mathbf{B}\,.\,\mathfrak{d}_m-\Sigma\mathrm{V}\mathfrak{q}_m\mathfrak{d}_m\,.\,\mathbf{B}$$
$$+\Sigma(\mathrm{V}\mathfrak{q}_m\mathfrak{d}_m)\mathbf{B}$$

$$=\mathbf{E}\,.\,\mathbf{D}+\mathbf{H}\,.\,\mathbf{B}-\tfrac{1}{2}\mathbf{E}\mathbf{D}-\tfrac{1}{2}\mathbf{H}\mathbf{B}+\Sigma\mathrm{V}\mathfrak{q}_m\mathbf{B}\,.\,\mathfrak{d}_m-\mathbf{H}\,.\,\mathbf{B}+\mathbf{H}\mathbf{B}$$

$$=\Sigma\{\mathbf{E}+\mathrm{V}\mathfrak{q}_m\mathbf{B}\,.\,\mathfrak{d}_m\}\qquad-\tfrac{1}{2}\mathbf{E}\mathbf{D}+\tfrac{1}{2}\mathbf{H}\mathbf{B}. \quad . \quad . \quad . \quad . \quad (35)$$

From (35)′ we see that the stress coincides with Maxwell's stress when there is no convection of momentum relative to the (so-called) fixed reference frame; and from (35) that it consists in general of a quasi-tension equal to $\mathbf{E}+\mathrm{V}\mathfrak{q}_m\mathbf{B}$ per tube of the mth set together with a hydrostatic pressure $\frac{1}{2}(\mathbf{E}\mathbf{D}-\mathbf{H}\mathbf{B})$. The torque per unit volume is seen to be

$$\phi-\phi'=\mathbf{S}=-\Sigma\mathrm{V}(\mathbf{E}+\mathrm{V}\mathfrak{q}_m\mathbf{B})\mathfrak{d}_m$$
$$=+\Sigma\mathrm{V}\mathfrak{d}_m\mathrm{V}\mathfrak{q}_m\mathbf{B}$$
$$=+\Sigma\mathrm{V}\mathfrak{q}_m\mathrm{V}\mathfrak{d}_m\mathbf{B}-\Sigma\mathrm{V}(\mathrm{V}\mathfrak{q}_m\mathfrak{d}_m)\mathbf{B}$$
$$=+\Sigma\mathrm{V}\mathfrak{q}_m\mathrm{V}\mathfrak{d}_m\mathbf{B}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

the last expression being the rate of change of moment of momentum about a fixed point due to component of velocity perpendicular to the momentum, familiar in the hydrodynamics of the motion of bodies in a fluid.

7. The flux of energy also consists of two parts: the convective flux due to the motion of the tubes, and the flux due to the activity of the stress. To find the convective flux we require to localize the energy in a manner rather difficult to justify. The whole energy per unit volume may be written

$$\tfrac{1}{2}\mathbf{N}\mathbf{B}+\tfrac{1}{2}\mathbf{E}\mathbf{D}$$
$$=\tfrac{1}{2}\Sigma\mathfrak{d}_m(\mathbf{E}-\mathrm{V}\mathfrak{q}_m\mathbf{B}). \quad . \quad . \quad . \quad . \quad (37)$$

Then we may suppose the part $\mathfrak{d}_m(\mathbf{E}-\mathrm{V}\mathfrak{q}_m\mathbf{B})$ of the energy to be moving with velocity $\mathfrak{q}_m$, and so on. The total convection of energy will therefore be

$$\tfrac{1}{2}\Sigma\mathfrak{d}_m(\mathbf{E}-\mathrm{V}\mathfrak{q}_m\mathbf{B})\,.\,\mathfrak{q}_m. \quad . \quad . \quad . \quad . \quad (38)$$

To find the stress-activity flux from (35), consider first the term $(\mathbf{E}+\mathrm{V}\mathfrak{q}_m\mathbf{B})\,.\,\mathfrak{d}_m$; the appropriate velocity is clearly $\mathfrak{q}_m$, and the flux (by Heaviside's method)

$$-\mathfrak{q}_m(\mathbf{E}+\mathrm{V}\mathfrak{q}_m\mathbf{B})\,.\,\mathfrak{d}_m=-\mathfrak{q}_m\mathbf{E}\,.\,\mathfrak{d}_m.$$

Again, we may write the second term

$$-\tfrac{1}{2}\mathbf{E}\mathbf{D}+\tfrac{1}{2}\mathbf{H}\mathbf{B}=-\tfrac{1}{2}\{(\Sigma\mathfrak{d}_m)\mathbf{E}-(\Sigma\mathrm{V}\mathfrak{q}_m\mathfrak{d}_m)\mathbf{B}\}$$
$$=-\tfrac{1}{2}\Sigma\mathfrak{d}_m(\mathbf{E}+\mathrm{V}\mathfrak{q}_m\mathbf{B}),$$

and it seems permissible to write the activity flux due to the term $-\frac{1}{2}\mathfrak{d}_m(\mathbf{E}+\mathrm{V}\mathfrak{q}_m\mathbf{B})$ as $+\frac{1}{2}\mathfrak{q}_m\,.\,\mathfrak{d}_m(\mathbf{E}+\mathrm{V}\mathfrak{q}_m\mathbf{B})$. Hence the

total activity flux will be

$$-\Sigma_i' \mathbf{q}_m \mathbf{E} \cdot \mathbf{d}_m - \tfrac{1}{2}\mathbf{d}_m(\mathbf{E} + V\mathbf{q}_m\mathbf{B})\}, \quad . \quad . \quad . \quad (39)$$

and the whole flux, adding (38) and (39),

$$\begin{aligned}\mathbf{W} &= \tfrac{1}{2}\Sigma \mathbf{d}_m(\mathbf{E} - V\mathbf{q}_m\mathbf{B}) \cdot \mathbf{q}_m - \Sigma \mathbf{q}_m \mathbf{E} \cdot \mathbf{d}_m + \tfrac{1}{2}\Sigma \mathbf{d}_m(\mathbf{E} + V\mathbf{q}_m\mathbf{B})\mathbf{q}_m \\ &= \Sigma(\mathbf{d}_m \mathbf{E} \cdot \mathbf{q}_m - \mathbf{q}_m \mathbf{E} \cdot \mathbf{d}_m) \\ &= V\mathbf{E}\Sigma V\mathbf{q}_m \mathbf{d}_m \\ &= V\mathbf{E}\mathbf{H}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)\end{aligned}$$

8. Since we have shown that this theory leads to the ordinary equations of the electromagnetic field, it is unnecessary to give a separate proof of the uniform propagation of disturbances with velocity $1/\sqrt{\mu}\mathrm{K}$. It is perhaps as well, however, to examine shortly the mechanism of propagation, particularly since the mental picture of electromagnetic radiation afforded by the theory is in many respects very satisfactory.

N. Campbell gives a short discussion of the question, and shows that a tube at rest may be compared to a flexible cord of linear density $\mu\mathrm{D}$ under a tension D/K; the square of the velocity of propagation of transverse disturbances being then $1/\mu\mathrm{K}$ by the elementary dynamics of cords. To extend this result to the case of a tube having a general velocity v perpendicular to its own direction, we have only to remember that, by equation (35) above, the stress to which the restoring force is due will now be the quasi-tension $\mathbf{E} + V\mathbf{q}\mathbf{B}$, where $\mathbf{q}$ is the velocity of the tubes, of which we shall suppose that only one set need be taken into account; and with this last assumption we may drop the suffix m and so write

$$\mathbf{B} = \mu V\mathbf{q}\mathbf{D}, \quad \mathbf{E} = \frac{\mathbf{d}}{\mathrm{K}}.$$

The $\mathbf{d}$ component of $\mathbf{E} + V\mathbf{q}\mathbf{D}$ is the only effective part of the stress, and its magnitude is given by

$$(\mathbf{E} + V\mathbf{q}\mathbf{B})\mathbf{d}_1 = \left(\frac{\mathbf{d}}{\mathrm{K}} + \mu V\mathbf{q}V\mathbf{q}\mathbf{d}\right)\mathbf{d}_1,$$

where $\mathbf{d}_1$ is the unit vector parallel to $\mathbf{d}$, or $\mathbf{d} = d\mathbf{d}_1$. This equals

$$\begin{aligned}&\frac{d}{\mathrm{K}}(1 + \mu\mathrm{K}\mathbf{d}_1 V\mathbf{q}V\mathbf{q}\mathbf{d}) \\ &= \frac{d}{\mathrm{K}}\{1 - \mu\mathrm{K}(V\mathbf{d}_1\mathbf{q})^2\} \\ &= \frac{d}{\mathrm{K}}\left\{1 - \frac{v^2}{c^2}\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)\end{aligned}$$

$c^2\mu\mathrm{K} = 1.$

The linear density will remain μd, so that the velocity of propagation along the tube will be $\sqrt{c^2-v^2}$. Since the tube itself is in motion with velocity v in a perpendicular direction, the propagation of the disturbance in space will be with velocity c in a direction making an angle $\sin^{-1}\frac{v}{c}$ with the tube. When $v=c$ the disturbance will not be propagated at all along the tube, which will lie in the wave-front ; and the traction $(\mathbf{E}+\mu\mathrm{V}\mathbf{q}\mathrm{V}\mathbf{q}\mathbf{D})$ will vanish.

9. To take into account a general velocity of the tube in the direction of its length, let us restrict ourselves to plane-polarized radiation. We shall take the x-axis in the direction of propagation, and the y-axis in that of the disturbance. Since we are dealing only with transverse vibrations, the velocity of the tubes in the direction of the ray will be constant from point to point along a tube. Let u be this x-component of velocity. Also let (x, y) be the coordinates of a point on some particular tube at time t, so that y is a function of x and t. Then the whole y-component of velocity of the point will be

$$v=\frac{dy}{dt}=\frac{\partial y}{\partial t}+u\frac{\partial y}{\partial x}. \quad . \quad . \quad . \quad . \quad . \quad (42)$$

It is obvious that the shearing motion perpendicular to the x-axis of the tubes in their vibration will not affect the number of tubes per unit area passing through a plane normal to the x-axis. Thus the quantity d_x, the x-component of electric displacement, will be constant at a point on the tube, or

$$\left(\frac{\partial}{\partial t}+u\frac{\partial}{\partial x}\right)d_x=0.$$

Also, if d_y is the y-component, we shall have

$$\frac{d_y}{d_x}=\frac{\partial y}{\partial x}.$$

And thus

$$d_y=\frac{\partial y}{\partial x}d_x,$$

$$d^2=d_x^2+d_y^2$$

$$=d_x^2\left\{1+\left(\frac{\partial y}{\partial x}\right)^2\right\}. \quad . \quad . \quad . \quad (43)$$

The momentum per unit length along the tube is

$$\mathrm{V}\mathbf{d}_1\mathbf{B}=\mu\mathrm{V}\mathbf{d}_1\mathrm{V}\mathbf{q}\mathbf{d}$$

$$=\mu(\mathbf{q}\,.\,d-\mathbf{d}\,.\,\mathbf{q}\mathbf{d}_1).$$

Multiply this by $\frac{d}{d_x}$ to find the value appropriate to unit length along the x-axis, and, taking the y-component, we have

$$\mu \frac{d}{d_x}\left[\left(\frac{\partial y}{\partial t}+u\frac{\partial y}{\partial x}\right)d-d_x\frac{\partial y}{\partial x}\frac{1}{d}\left\{ud_x+\left(\frac{\partial y}{\partial t}+u\frac{\partial y}{\partial x}\right)d_x\frac{\partial y}{\partial x}\right\}\right]$$

$$=\mu d_x\left[\left(\frac{\partial y}{\partial t}+u\frac{\partial y}{\partial x}\right)\frac{d^2}{d_x^2}-\frac{\partial y}{\partial x}\left\{u+\left(\frac{\partial y}{\partial t}+u\frac{\partial y}{\partial x}\right)\frac{\partial y}{\partial x}\right\}\right]$$

$$=\mu d_x\times$$

$$\left[\frac{\partial y}{\partial t}\left\{1+\left(\frac{\partial y}{\partial x}\right)^2-\left(\frac{\partial y}{\partial x}\right)^2\right\}+u\frac{\partial y}{\partial x}\left\{1+\left(\frac{\partial y}{\partial x}\right)^2-1-\left(\frac{\partial y}{\partial x}\right)^2\right\}\right]$$

$$=\mu d_x\frac{\partial y}{\partial t}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

Hence the rate of change of momentum in the y-direction per unit length along the x-axis is

$$\left(\frac{\partial}{\partial t}+u\frac{\partial}{\partial x}\right)\mu d_x\frac{\partial y}{\partial t}=\mu d_x\left[\frac{\partial^2 y}{\partial t^2}+u\frac{\partial^2 y}{\partial x\partial t}\right]. \quad . \quad (45)$$

The force to be equated to this arises from the quasi-tension

$$\mathbf{E}+\mathrm{V}\mathbf{q}\mathbf{B}=\frac{\mathbf{d}}{\mathrm{K}}+\mu\mathrm{V}\mathbf{q}\mathrm{V}\mathbf{q}\mathbf{D}$$

$$=\frac{\mathbf{d}}{\mathrm{K}}+\mu\mathbf{q}\,.\,\mathbf{q}\mathbf{d}-\mu\mathbf{d}\,.\,\mathbf{q}^2,$$

of which the y-component is

$$\frac{1}{\mathrm{K}}d_x\frac{\partial y}{\partial x}+\mu\left(\frac{\partial y}{\partial t}+u\frac{\partial y}{\partial x}\right)\left\{ud_x+\left(\frac{\partial y}{\partial t}+u\frac{\partial y}{\partial x}\right)d_x\frac{\partial y}{\partial x}\right\}$$

$$-\mu d_x\frac{\partial y}{\partial x}\left\{u^2+\left(\frac{\partial y}{\partial t}+u\frac{\partial y}{\partial x}\right)^2\right\}$$

$$=\frac{1}{\mathrm{K}}d_x\frac{\partial y}{\partial x}+\mu\left(\frac{\partial y}{\partial t}+u\frac{\partial y}{\partial x}\right)ud_x-\mu d_x\frac{\partial y}{\partial x}u^2$$

$$=\frac{1}{\mathrm{K}}d_x\frac{\partial y}{\partial x}+\mu d_x u\frac{\partial y}{\partial t}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

Differentiating with respect to x we have the force per unit length

$$d_x\left[\frac{1}{\mathrm{K}}\frac{\partial^2 y}{\partial x^2}+\mu u\frac{\partial^2 y}{\partial x\partial t}\right] \quad . \quad . \quad . \quad . \quad (47)$$

Equating therefore expressions (45) and (47) and dividing by d_x, we have

$$\frac{1}{\mathrm{K}}\frac{\partial^2 y}{\partial x^2}+\mu u\frac{\partial^2 y}{\partial x\partial t}=\mu u\frac{\partial^2 y}{\partial x\partial t}+\mu\frac{\partial^2 y}{\partial t^2},$$

or

$$\frac{\partial^2 y}{\partial t^2}=c^2\frac{\partial^2 y}{\partial x^2}, \quad . \quad . \quad . \quad . \quad . \quad (48)$$

exhibiting the uniform propagation with velocity c independent of the general motion of the tube.

The relation between the electromagnetic disturbance and the displacement y of the tube is easily seen to be given by

$$\mathrm{E}_y=\frac{d_y}{\mathrm{K}}=\frac{1}{\mathrm{K}}d_x\frac{\partial y}{\partial x} \quad . \quad . \quad . \quad . \quad . \quad (49)$$

$$\mathrm{H}_z=-\frac{\partial y}{\partial t}d_x$$

$$=\frac{1}{\mu c}\mathbf{E}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50)$$

But while in plane-polarized radiation the displacement of the tube from its normal position is thus perpendicular to the plane of polarization, in circularly polarized rays it is easy to see that the reverse is the case.

10. The intention in presenting the theory of Faraday tubes in the present form was to suggest possibilites of modification which might explain various phenomena of which no entirely satisfactory electrical explanation has been given so far.

In making attempts of this kind we may, for instance, take advantage in various ways of the fact that the electric displacement has been considered as a mean value taken over a small, but not infinitesimal, area. From this point of view the Maxwellian theory is microscopical, and a more microscopical theory may be what is required in various regions of modern physics.

Again, the present theory rests on the localization of electric and magnetic energy as functions of **D** and **H** and on the derivation from these of equations of motion. Hence it would be comparatively simple to estimate the effects either of a modified distribution of energy, or of substituting any different hypothesis for the principle of action.

Lastly, quite a variety of hypotheses are possible as to the exact nature of the electric particles.

11. It will be observed that in describing the properties of

the tubes of force we have so far assumed that two oppositely directed tubes at the same point exactly cancel each other in their effects, if they are moving with the same velocity. Now, just as the electrical theory of matter explains all the phenomena of neutral bodies as due to the existence of the equal mixture of positive and negative electricity, which on the two-fluid theory was supposed to have no recognizable physical properties, so on the lines of force theory we may perhaps speculate with advantage on the possibility of explaining by means of properties of equal mixtures of oppositely directed tubes the phenomenon of gravitation, which seems for many reasons to be on a different level from the ordinary electrical phenomena. Let us consider the potential energy of such a mixture of tubes. So long as we choose an element of area large enough to include many tubes, the density of energy $\frac{1}{2}$ED must always vanish ; but as we take smaller and smaller elements of area, there will be an increasing probability of the number of tubes passing through it in one direction being not quite equal to the number passing through it in the opposite direction : in other words, what to ordinary microscopic electrical measurements is a uniform absence of electric displacement may consist of alternate regions of opposite displacement so small that only the mean field of a considerable number of regions is measured. Such a field would have positive potential energy ; but since the more closely the tubes are packed, the smaller is the element of area we can take without considering this effect, it seems reasonable to suppose that the effect will become smaller the more numerous are the tubes of either sign. Not improbably a mathematical form might be given to this hypothesis which would explain and locate the energy of gravitation. Let de_1, $-de_1$; de_2, $-de_2$, be pairs of opposite charges ; r_1, r_2 the (small) distances apart of the components of each pair ; and R the distance between the pairs. Then if the hypothesis could be so formulated that the potential energy of the system would include a term of the form

$$-\gamma \frac{de_1^2 de_2^2}{r_1 r_2 \mathrm{R}},$$

where γ is a positive constant, the law of gravitation would be completely satisfied, and gravitational mass would be identified exactly with electromagnetic mass ; for

$$\frac{de_1^2}{r_1}$$

is proportional to the element of electromagnetic mass due to two elements of de_1, $-de_1$.

This last question is of some interest in the theory of atomic structure; a number of writers have laid stress on the importance of mutual electromagnetic mass, and in particular Harkins and E. D. Wilson * have used this phenomenon to explain the departure of atomic *weights* from whole numbers. It appears, however, that such an explanation could alone be valid if mutual mass were ponderable.

12. The theory of Faraday tubes might possibly be employed with advantage in other investigations connected with atom theory. Sir J. J. Thomson † has made several suggestions of this nature; his conception of the electron as possibly simply the end of a single Faraday tube would, of course, have very important consequences if adhered to in any theory of atomic structure.

Again, if we suppose that electrons and positive nuclei have the property of excluding the tubes of other electrons and nuclei, the attractions between particles of opposite sign would become a repulsion at very small distances. Or we may suppose that some or all of the tubes of an electron in an atom simply end at a nucleus, instead of spreading equally outwards in all directions; and different states of an atom, with different periods of vibration, might arise according to the number of tubes so connected. Suggestions have also been made as to the application of the theory in connexion with a possible discrete structure in radiation ‡.

Conclusion.

13. It has been shown that the general equation of the Maxwell-Lorentz-Heaviside theory of electromagnetism can be derived as macroscopic consequences of a simple dynamical theory of Faraday tubes.

This theory also gives explicit and non-contradictory expression to the ideas of electromagnetic stress, momentum, and flux of energy, and an electromechanical picture of radiation explaining the law of uniform propagation in spite of the motion of the source.

A number of suggestions are made as to applications to the theory of gravitation and other problems.

Hawke Battalion,
Royal Naval Division.

* Phil. Mag. Nov. 1915, p. 723.

† Phil. Mag. (6) xxvi. p. 792.

‡ Jeans, "Report on Quantum Theories," Proc. Lond. Phys. Soc., 1915.

LV. *Molecular Thermodynamics.* III. *By* Bernard A. M. Cavanagh, *B.A., Balliol College, Oxford* *.

Solvation of Solutes.

THE partial solvation of a solute—that is, the combination of some fraction of it with the substance which, in the free state, constitutes the solvent—to form a "solvate" or "solvates" is a phenomenon probably of the very widest prevalence in solutions, particularly in our more common and valuable solvents. It has unfortunately been too readily ignored, because in dilute solutions its effects are not of the first order of magnitude. They are nevertheless considerable, in many cases much more considerable than has generally been allowed for; and, in any attempt to pass beyond the region of the most dilute solutions (say, $\frac{M}{50}$), the question of solvation of the solutes must receive very serious consideration.

In the present treatment, it is to be understood, the "solvates" considered are true chemical compounds, at any rate in the one sense required by molecular thermodynamics †, and the conclusions reached are not to be expected to apply in any degree to any other "associations" or "complexes" to which the name "solvate" might be given.

The following are the general circumstances considered here:—

Any number of "solutes" dissolved in a complex ‡ solvent are indefinitely solvated, without dissociation or association—that is to say, each forms one unsolvated molecular species and any number of solvate-species by combination of one unsolvated molecule with different amounts of solvent.

The residual solvent not so "absorbed" by combination with the solutes may be called the "free solvent" §.

The separable or experimental solutes have been called the "unsolvated" solutes, and it would appear a little paradoxical to say that these may be solvates; but, in fact,

* Communicated by Dr. J. W. Nicholson, F.R.S.

† See second paper, Phil. Mag. xliv. p. 229 (1922), 1st section.

‡ See second paper, *loc. cit.* The case where the solvent is simple is included as a limiting case.

§ In the previous paper the term "solvent" was used to signify "free solvent," since the combined or "bound" solvent was not there under consideration.

the treatment below will apply in full and without alteration in such a case, if a lower solvate be regarded as a "negative" solvate of a higher.

The following alternative and more general statement of the problem will make this clearer :—

The molecular species present in the phase or solution are the several solvent-molecular species which together constitute the "free solvent" and a number of solute-molecular species. Now the latter can be grouped in such a way that members of a group differ in composition only in the amount of solvent per molecule, and can be regarded as positive or negative solvates of one another. One member of each group appears in the present discussion as a separable or "experimental" solute—a component under the conditions of experiment : and the (positive or negative) quantities of solvent by which the other members differ from this one are, and are alone, regarded as "bound" solvent, which together with the "free" comprises the "total solvent."

In the "molecular" expression for ψ, from which we started in the previous paper, every molecular species appears as a component. In the "experimental" expression obtained in that paper the free solvent appears as one component only, and in the present paper, starting from this result, which we may refer to as our "original" expression for ψ, we shall obtain an expression in which the "total solvent" and the "unsolvated solutes" are the components.

It is clear that problems, such as dissociation and combination of the solutes, excluded from present consideration, can be treated as further stages in this gradual reduction of the components.

Let M_0 be the mass of free solvent considered, and M_0' that of the total solvent, the latter but not the former being an experimental (known and controllable) quantity.

Concentrations referred to the latter may be called "experimental" concentrations,

$$c_s' = \frac{n_s}{M_0'}, \quad C' = \frac{\Sigma n_s}{M_0'} = \frac{N}{M_0'}, \quad . \quad . \quad . \quad . \quad (1)$$

while those referred to the former,

$$c_s = \frac{n_s}{M_0}, \quad C = \frac{\Sigma n_s}{M_0} = \frac{N}{M_0}, \quad . \quad . \quad . \quad . \quad (2)$$

may be called "true" concentrations. The latter alone were used in the consideration of "complex solvents."

It will be a convenience making for clarity, to obtain

our results in the first place in terms of the "true concentrations," introducing the "experimental" concentrations afterwards.

Of the total number n_s of gm.-molecules of the solute, (s), put into the solution, let the fractions x_{s_1}, x_{s_2}, ..., go to form solvates containing respectively M_{s_1}, M_{s_2}, ..., *grams* of solvent per gram-molecule, and let us write X_s for Σx_{s_1}, and α_s for $\Sigma x_{s_1} M_{s_1}$; then clearly (from previous paper) our "original" expression for ψ is

$$\psi = M_0\left[\phi_M + R\int_{C=0}^{\bar{m}} \frac{1}{\bar{m}}\, d\log(1+\bar{m}C)\right] + \Sigma n_s\left\{(1-X_s)\left[\phi_{s_0} - R\log\frac{c_s(1-X_s)}{\frac{\bar{m}_0}{\bar{m}} + \bar{m}_0 C}\right] + \Sigma x_{s_1}\left[\phi_{s_1} - R\log\frac{c_s x_{s_1}}{\frac{\bar{m}_0}{\bar{m}} + \bar{m}_0 C}\right]\right\} + M_0 G', \quad (3)$$

and is of the form

$$\psi = M_0\frac{\partial\psi}{\partial M_0} + \Sigma n_s(1-X_s)\frac{\partial\psi}{\partial n_{s_0}} + \Sigma\Sigma n_s x_{s_1}\frac{\partial\psi}{\partial n_{s_1}}, \quad . \quad (4)$$

the independent variables being M_0, $n_s(1-X_s)$, $n_s x_{s_1}$, $n_s x_{s_2}$, ...

The "experimental" expression for ψ, now required, must have the form

$$\psi = M_0'\frac{\partial\psi}{\partial M_0'} + \Sigma n_s\frac{\partial\psi}{\partial n_s}, \quad . \quad . \quad . \quad . \quad (5)$$

the independent variables being M_0', n_s, ...

In changing the variables we make use of the equations given by the chemical equilibrium governing the various stages of solvation, viz.:

$$\left.\begin{aligned}\frac{\partial\psi}{\partial n_{s_1}} - \frac{\partial\psi}{\partial n_{s_0}} - M_{s_1}\frac{\partial\psi}{\partial M_0} = 0,\\ \frac{\partial\psi}{\partial n_{s_2}} - \frac{\partial\psi}{\partial n_{s_0}} - M_{s_2}\frac{\partial\psi}{\partial M_0} = 0,\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (6)$$

etc.,

whence, of course,

$$\Sigma x_{s_1}\frac{\partial\psi}{\partial n_{s_1}} - X_s\frac{\partial\psi}{\partial n_{s_0}} - \alpha_s\frac{\partial\psi}{\partial M_0} = 0, \quad . \quad . \quad . \quad . \quad (7)$$

and similarly

$$\Sigma \frac{\partial \Psi}{\partial n_{s_1}} dx_{s_1} + \frac{\partial \Psi}{\partial n_{s_0}} d(1-X_s) - \frac{\partial \Psi}{\partial M_0} d\alpha_s = 0, \quad . \quad (8)$$

whereby the (somewhat lengthy) full differentiation of (3) with respect to the new variables reduces to

$$\frac{\partial \Psi}{\partial M_0'} = \frac{\partial \Psi}{\partial M_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\frac{\partial \Psi}{\partial n_s} = \Sigma x_{s_1} \frac{\partial \Psi}{\partial n_{s_1}} + (1-X_s) \frac{\partial \Psi}{\partial n_{s_0}} - \alpha_s \frac{\partial \Psi}{\partial M_0}, \quad . \quad (10)$$

$$= \frac{\partial \Psi}{\partial n_{s_0}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

equations of obvious physical significance.

Now (11) with (3) gives

$$\left[\frac{\partial \Psi}{\partial n_s} + R \log c_s\right] = \phi_{s_0} - R \log (1-X_s) + R \log \left(\frac{\overline{m}_0}{\overline{m}} + \overline{m}_0 C\right) + G_{s_0}' \quad (12)$$

and

$$\operatorname*{Lt}_{C \to 0} \left[\frac{\partial \Psi}{\partial n_s} + R \log c_s\right] = \phi_{s_0} - R \log (1-X_{s_0}) = \phi_s \text{ (say)}, \quad (13)$$

since X_{s_0}, or $\operatorname*{Lt}_{C \to 0} X_s$, depends only on temperature and pressure.

Then

$$\left[\frac{\partial \Psi}{\partial n_s} + R \log c_s\right] = \phi_s + \int_{C=0}^{\cdot} d\left[\frac{\partial \Psi}{\partial n_s} + R \log c_s\right],$$

i.e.

$$\frac{\partial \Psi}{\partial n_s} = \phi_s - R \log c_s + \int_{C=0} d\left[\frac{\partial \Psi}{\partial n_s} + R \log c_s\right]. \quad . \quad (14)$$

On the one hand, of course,

$$\frac{\partial \Psi}{\partial n_s} = \left[\phi_s - R \log \frac{c_s}{\frac{\overline{m}_0}{\overline{m}} + \overline{m}_0 C} - R \log \frac{1-X_s}{1-X_{s_0}}\right] + G_{s_0}'; \quad (15)$$

but, on the other hand, from (8) and (10) we get

$$d\left(\frac{\partial \Psi}{\partial n_s}\right) = \Sigma x_{s_1} d\left(\frac{\partial \Psi}{\partial n_{s_1}}\right) + (1-X_s) d\left(\frac{\partial \Psi}{\partial n_{s_0}}\right) - \alpha_s d\left(\frac{\partial \Psi}{\partial M_0}\right), \quad (16)$$

and, referring to (3), while remembering

$$\Sigma x_{s_1} + (1 - X_s) = 1,$$

$$\Sigma x_{s_1} d \log x_{s_1} + (1 - X_s) d \log (1 - X_s) = 0,$$

we obtain

$$d\left[\frac{\partial \psi}{\partial n_s} + R \log c_s\right] \quad \ldots \rightarrow$$

$$= R\left[d \log \left(\frac{\overline{m}_0}{\overline{m}} + \overline{m}_0 C\right) - \frac{\alpha_s}{\overline{m}} d \log (1 + \overline{m} C)\right]$$

$$+ \Sigma x_{s_1} d G_{s_1}' + (1 - X_s) d G_{s_0}' - \alpha_s d G_M' ; \quad (17)$$

whence (14) gives, as alternative to (15),

$$\frac{\partial \psi}{\partial n_s} = \phi_s - R\left[\log \frac{c_s}{\frac{\overline{m}_0}{\overline{m}} + \overline{m}_0 C} + \int_{C=0}^{C} \frac{\alpha_s}{\overline{m}} d \log (1 + \overline{m} C)\right] + G_s, \quad \ldots \quad (18)$$

where

$$G_s = \int_{C=0}^{C} [(1 - X_s) d G_{s_0}' + \Sigma x_{s_1} d G_{s_1}' - \alpha_s d G_M'] \ldots \quad (19)$$

Comparing (15) and (18), we obtain

$$R \log \frac{1 - X_s}{1 - X_{s_0}} = R \int_{C=0}^{C} \frac{\alpha_s}{\overline{m}} d . \log (1 + \overline{m} C) - (G_s - G_{s_0}), \ldots \quad (20)$$

or

$$R d \log (1 - X_s) = R \frac{\alpha_s}{\overline{m}} d \log (1 + \overline{m} C)$$

$$+ [\alpha_s d G_M' + X_s d G_{s_0}' - \Sigma x_{s_1} d G_{s_1}'], \quad (21)$$

which could be obtained independently from (7) and (8) with (3), and then used to get (18) from (15) : but the above derivation from the physically significant equation (10) appeared more interesting, and brings out an analogy with the previous problem of "complex solvents."

When there is present only one solute (s) (but any number of solvates thereof), (18) can also be obtained easily, by means of the Gibbs fundamental relation, from $\frac{\partial \psi}{\partial \overline{M}_0}$.

The general terms being G_s in (18) and G_{s_0}' in (15) we see that the division into "linear" and "general"

terms is different in the two expressions for $\frac{\partial\psi}{\partial n_s}$, the difference being the quantity

$$G_s - G_{s_0}' = \int_{C=0}^{\infty} \Sigma x_{s_1} d[G_{s_1}' - G_{s_0}' - M_{s_1} G_M'] . \quad . \quad (22)$$

The form (18) will probably be the more generally useful, possessing the advantage that the "linear" and "general" terms separately are connected by the Gibbs fundamental relation with those (respectively) in the simple form of $\frac{\partial\psi}{\partial M_0'}$,

$$\frac{\partial\psi}{\partial M_0'} = \frac{\partial\psi}{\partial M_0} = \left[\phi_M + R\int_{C=0}^{\infty} \frac{1}{m} d\log(1+\overline{m}C)\right] + G_M' . \quad (23)$$

For since (*cf.* (3), (4), and previous paper)

$$M_0 dG_M' + \Sigma n_s (1 - X_s) dG_{s_0}' + \Sigma\Sigma n_s x_{s_1} dG_{s_1}' = 0 \quad . \quad (24)$$

and

$$M_0 = M_0' - \Sigma n_s \alpha_s , \quad . \quad . \quad . \quad . \quad . \quad (25)$$

clearly

$$M_0' dG_M' + \Sigma n_s [(1 - X_s) dG_{s_0}' + \Sigma x_{s_1} dG_{s_1}' - \alpha_s dG_M'] = 0, \quad (26)$$

i. e. $$M_0' dG_M' + \Sigma n_s dG_s = 0 ; \quad . \quad . \quad . \quad (27)$$

so that, if G is a function of c_1', c_2', ("experimental" concentrations), such that

$$M_0' G = M_0' G_M' + \Sigma n_s G_s , \quad . \quad . \quad . \quad . \quad (28)$$

we have

$$G_s = \left(\frac{\partial M_0' G}{\partial n_s}\right)_{M_0'}^{*} = \frac{\partial G}{\partial c_s'}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

$$G_M' = \left(\frac{\partial M_0' G}{\partial M_0'}\right)_n \quad [= G_M \text{ (say)}] = G - \Sigma c_s' \frac{\partial G}{\partial c_s'} . \quad (30)$$

Now G′ is a function of $c_1, c_2, \ldots\ldots$ and also of the various fractions $x_{1_1}, x_{1_2}, \ldots\ldots, x_{s_1}, x_{s_2}, \ldots\ldots$ If we take the quantity $\frac{M_0}{M_0'} G'$, and eliminate the "true" concentrations (C, c_s) by

* This common usage of the suffix outside the bracket was mentioned in the previous paper. n here indicates constancy of all the n's and x (later) constancy of all the x's.

means of the relations

$$1-\Sigma c_s'\alpha_s = \frac{M_0}{M_0'} = \frac{c_s'}{c_s} = \frac{C'}{C}, \quad . \quad . \quad . \quad . \quad (31)$$

we obtain a function (say, G'') of the "experimental" concentrations (C', c_s') and of the various x's, as independent variables, and clearly

$$\frac{\partial G''}{\partial c_s'}\left[=\left(\frac{\partial G''}{\partial c_s'}\right)_x=\left(\frac{\partial M_0'G''}{\partial n_s}\right)_{M_0',\,x}\right]=\left(\frac{\partial M_0G'}{\partial n_s}\right)_{M_0',\,x}$$

$$=G_{s_0}'\left[\frac{\partial n_s(1-X_s)}{\partial n_s}\right]_x+\Sigma G_{s_1}'\left(\frac{\partial n_s x_{s_1}}{\partial n_s}\right)_x+G_M'\left(\frac{\partial M_0}{\partial n_s}\right)_{M_0',\,x}$$

$$=(1-X_s)G_{s_0}'+\Sigma x_{s_1}G_{s_1}'-\alpha_s G_M', \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

for which we may therefore write G_s'', so that

$$M_0'G'' = M_0'G_M' + \Sigma n_s G_s''. \quad . \quad . \quad . \quad . \quad (33)$$

On the other hand,

$$\frac{\partial G''}{\partial x_{s_1}}\left[=\frac{1}{M_0'}\left(\frac{\partial M_0'G''}{\partial x_{s_1}}\right)_{M_0',\,n}\right]=\frac{1}{M_0'}\left(\frac{\partial M_0G'}{\partial x_{s_1}}\right)_{M_0',\,n}$$

$$=\frac{1}{M_0'}\left[G_{s_1}'\left(\frac{\partial n_s x_{s_1}}{\partial x_{s_1}}\right)_n+G_{s_0}'\left(\frac{\partial n_s(1-X_s)}{\partial x_{s_1}}\right)_n\right.$$

$$\left.+G_M'\left(\frac{\partial M_0}{\partial x_{s_1}}\right)_{M_0',\,n}\right]$$

$$=c_s'\left[G_{s_1}'-G_{s_0}'-M_{s_1}G_M'\right]=c_s'G_{x_{s_1}}'' \text{ (say)}. \quad . \quad (34)$$

(19), (32), and (34) then give

$$G_s = G_s''-\int_{C=0}^{\cdot}\Sigma G_{xs_1}''dx_{s_1}$$

$$=\frac{\partial G''}{\partial c_s'}-\int_{C=0}^{\cdot}\frac{1}{c_s'}\Sigma\frac{\partial G''}{\partial x_{s_1}}dx_{s_1}; \quad . \quad . \quad . \quad (35)$$

and therefore from (28)

$$G = G''-\Sigma c_s'\int_{C=0}^{\cdot}\Sigma G_{x_{s_1}}''dx_{s_1}$$

$$=G''-\Sigma c_s'\int_{C=0}^{\cdot}\frac{1}{c_s'}\Sigma\frac{\partial G''}{\partial x_{s_1}}dx_{s_1}, \quad . \quad . \quad . \quad (36)$$

(35) and (36) being plainly in accord, as they must be, with (29).

Our final "experimental" expression for ψ, in terms of "true" concentrations, is

$$\psi = M_0' \left[\phi_M + R \int_{C=0}^{\bullet} \frac{1}{\bar{m}} d \log (1 + \bar{m}C) \right]$$

$$+ \Sigma n_s \left[\phi_s - R \left\{ \log \frac{c_s}{\frac{\bar{m}_0}{\bar{m}} + \bar{m}_0 C} \right.\right.$$

$$\left.\left. + \int_{C=0}^{\bullet} \frac{\alpha_s}{\bar{m}} d \log (1 + \bar{m}C) \right\} \right] + M_0' G, \quad (37)$$

where G has some form

$$G = R \Sigma \phi_x' f_x (c_1' c_2' \ldots\ldots). \quad . \quad . \quad . \quad . \quad (38)$$

The "general" terms in the original equation (3) were $M_0 G'$—that is, $M_0' G''$; so that the quantity

$$\Sigma n_s \int_{C=0}^{\bullet} \Sigma G_{x_{s_1}}'' dx_{s_1} \quad \text{or} \quad \Sigma n_s \int_{C=0}^{\bullet} \frac{1}{c_s'} \Sigma \frac{\partial G''}{dx_{s_1}} dx_{s_1} \quad . \quad (39)$$

has passed from "general" to "linear" terms in ψ; or, in $\frac{\partial \psi}{\partial n_s}$, the quantity

$$G_{s_1}'' - G_s = \int_{C=0} \Sigma G_{x_{s_1}}'' dx_{s_1}. \quad . \quad . \quad . \quad . \quad (40)$$

We may recall at this point equation (22), which is now

$$G_s - G_{s_0}' = \int_{C=0} \Sigma x_{s_1} d G_{x_{s_1}}'', \quad . \quad . \quad . \quad . \quad . \quad (41)$$

and note that, disregarding (more or less fortuitous) cancellation, the condition for the vanishing of (40) and (41) is *quditatively* the same, viz., that G'' shall be independent of the extent of solvation of the solute (*s*)—an obvious particular case being "Perfect Solution," where G'' vanishes.

The lack of practical significance in such a qualitative statement is illustrated and emphasized when we observe that *quantitatively* the condition is very different in the two cases. The two differences (40) and (41) are, in fact, complementary parts of the quantity

$$\Sigma x_{s_1} G_{x_{s_1}}'' = (G_s'' - G_{s_0}'), \quad . \quad . \quad . \quad . \quad (42)$$

and since

$$\int_{C=0} dG_{x_{s_1}}'' = G_{x_{s_1}}'',$$

whereas $\int_{C=0} dx_{s_1}$ will be only some fraction—generally, as we shall see, not large—of x_{s_1}, a simple graphical consideration will suffice to show that (41) will generally be much greater than (40).

The practical significance and value of the quantitative statement (39) is further illustrated in Appendix II.

The analogy between the modification of the "general" terms, expressed in (39), and that found necessary in the previous treatment of "complex solvents" is plain. In the latter we kept

$$G_s = G_s',$$

whereas in the present case we have kept

$$G_M = G_M',$$

but, of course, since we started in the present case from the results of the previous paper (and G′ in this paper corresponds to G in the previous paper), the two modifications of the "general" terms in the "molecular" expression are, as it were, superimposed.

More detailed treatment than the above of the "general" terms will be possible only when something is known about their form (see, for instance, Appendix II.).

For the evaluation of the linear terms we observe that α_s must be expressed as a function of the concentrations of the solutes.

An Expansion of α_s.

Consider, first, a solute which forms only one solvate. In this case we can write x_s, M_s, etc., instead of x_{s_1}, M_{s_1}, etc., and, moreover, we have

$$\left.\begin{aligned} \alpha_s &= M_s x_s \\ X_s &= x_s \\ X_{s_0} &= x_{s_0} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (43)$$

and equation (21) assumes the form,

$$R d \log (1 - x_s) = x_s \left[R \frac{M_s}{m} d \log (1 + \overline{m} C) - d G_{x_s}'' \right], \quad (44)$$

or if we write

$$y = \left[M_s \int_{C=0}^{C} \frac{1}{m} d \log (1 + \overline{m}C) - \frac{1}{R} G_{x_s}'' \right], \quad . \quad (45)$$

then

$$\frac{d}{dy}(1 - x_s) = x_s(1 - x_s). \quad . \quad . \quad . \quad . \quad . \quad (46)$$

If now we write x_s as a series of ascending integral powers of y, we can show that a few terms only need be taken for our practical purposes *, so long as y is little greater than unity—that is, we obtain a practical expression for x_s which will serve up to very high concentrations.

Putting then

$$x_s = x_{s_0} + b_1 y + b_2 y^2 + b_3 y^3 + \ldots + b_n y^n \ldots$$

by straightforward substitution in (45) (and equating coefficients) we obtain b_1, b_2, ... in terms of x_{s_0}.

A simple relation between these coefficients enables them to be written down very easily, viz.:

$$n b_n = b_1 \frac{d}{d x_{s_0}} b_{n-1},$$

the first coefficient b_1 being $x_{s_0}(x_{s_0} - 1)$, and being a factor of all the others. The alternate coefficients are also divisible by $(x_{s_0} - \frac{1}{2})$.

The numerical values of the coefficients depend, of course, on that of x_{s_0} which may be any proper fraction (positive). Their maximal (absolute) values can be obtained and shown to decrease rather rapidly. The higher members of the series have, of course, several maxima, but the *greatest* maximal (absolute) values diminish by alternate long and short steps, the following round values being sufficient for present consideration:

b_1.	b_2.	b_3.	b_4.	b_5.	b_6.	b_7.
$\frac{1}{4}$	$\frac{1}{22}$	$\frac{1}{48}$	$\frac{1}{300}$	$\frac{1}{480}$	—	$\frac{1}{4400}$.

Taking $\frac{1}{5}$ per cent. as our standard of experimental accuracy, we see that the series as far as y^3,

$$x_s = x_0 + b_1 y + b_2 y^2 + b_3 y^3, \quad . \quad . \quad . \quad . \quad . \quad (47)$$

will suffice until y closely approaches unity, when the y^4 term will be just appreciable.

* That is, the remainder after a few terms is negligible experimentally up to high concentrations. We may conveniently call this "converging practically up to high concentrations."

We have then α_s as a practical function of y, which is a function of the concentrations of the solutes (see (44)), and if we know the form of G_{x_s}'' we can readily complete the evaluation of $\int_{C=0}^{C} \frac{\alpha_s}{\overline{m}} d \log (1+\overline{m}C)$.

First, let us assume that $\overset{x_s}{\underset{R}{}} G_{x_s}''$ can be neglected and write

$$y = M_s \int_{C=0}^{C} \frac{1}{\overline{m}} d \log (1+\overline{m}C).$$

From the previous paper we can then write,

$$y = M_s C[1 - \tfrac{1}{2}a_1 C + \tfrac{1}{3}a_2 C^2 - \tfrac{1}{4}a_3 C^3],$$

and from (43) and (47) we then get

$$\alpha_s = \alpha_{s_0} + \beta_s C + \gamma_s C^2 + \delta_s C^3. \quad . \quad . \quad . \quad . \quad (48)$$

Where

$$\left.\begin{array}{ll} \alpha_{s_0} = M_s x_{s_0}, & \gamma_s = (b_2 M_s^3 - \tfrac{1}{2}a_1 b_1 M_s^2), \\ \beta_s = M_s^2 b_1, & \delta_s = (b_3 M_s^4 - a_1 b_2 M_s^3 + \tfrac{1}{3}a_2 b_1 M_s^2) \end{array}\right\}, \quad (49)$$

which may be expected to hold up to a value of C rather higher than $\frac{1}{M_s}$ (since y is considerably less then $M_s C$ at high concentrations), that is, in aqueous solution for example, up to a total concentration ("true") of at least twelve-molar (12M.) when the solvate is a pentahydrate, or six-molar (6M.) when it is a decahydrate.

When $\overset{x_{s_0}}{\underset{R}{}} G_{x_s}''$ is not negligible the above will cease to hold exactly, but it may be possible to express $\overset{x_{s_0}}{\underset{R}{}} G_{x_s}''$ (with a negligible residual error) as a function of C, the total solute concentration, and if this function can approximately take the form of a short series of integral powers we shall get a result in the above form, (48), but with departures in the values of the coefficients γ_s and δ_s.

When the solute considered forms several solvates, the problem of obtaining α_s as a function of the concentrations is more complex. Equation (21) takes the form

$$d \log (1 - X_s) = \Sigma x_{s_1} \left[\frac{M_s}{\overline{m}} d \log (1+\overline{m}C) - \frac{1}{R} d G_{x_{s_1}}'' \right]; \quad (50)$$

but we now have to use instead the series of equations (6)

from which, as already remarked, (21) might have been directly obtained, and which can be written

$$\left.\begin{aligned} d\log\frac{1-X_s}{x_{s_1}} &= M_{s_1}(1-\tfrac{1}{2}a_1C+\tfrac{1}{3}a_2C^2-\tfrac{1}{4}a_3C^3)dC-\frac{1}{R}dG_{x_{s_1}}'' \\ d\log\frac{1-X_s}{x_{s_2}} &= M_{s_2}(1-\tfrac{1}{2}a_1C+\tfrac{1}{3}a_2C^2-\tfrac{1}{4}a_3C^3)dC-\frac{1}{R}dG_{x_{s_2}}'' \\ &\text{(and so on).} \end{aligned}\right\} \quad (51)$$

Again, we pass over the most general case, where it is necessary to consider $G_{x_{s_1}}''$, etc., as depending in specific ways upon the particular solutes present, and we suppose (except for negligible residues) $G_{x_{s_1}}''$, etc., can be accounted for as functions of C. If these functions can be written approximately as short series of integral powers, then the above equations will take the general forms,

$$\left.\begin{aligned} d\log\frac{1-X_s}{x_{s_1}} &= [g_0+g_1C+g_2C^2+g_3C^3\ldots\ldots]dC \\ d\log\frac{1-X_s}{x_{s_2}} &= [g_0'+g_1'C+g_2'C^2+g_3'C^3\ldots\ldots]dC \\ &\text{etc.} \end{aligned}\right\}, \quad (52)$$

whence x_{s_1}, x_{s_2}, ... (and so α_s), can all be obtained in the form of ascending series of integral powers of C, by a procedure entirely analogous to that used in the simpler case of one solvate, viz., by assuming such forms for x_{s_1}, x_{s_2}, ..., and then determining the coefficients in terms of g_0, g_1, g_2, ..., by substituting in the above equations used of course simultaneously.

The interesting simple case where there are two solvates and $G_{x_{s_1}}''$, $G_{x_{s_2}}''$ can be neglected, has been investigated and it has been found, as might be anticipated, that in the expression for α_s,

$$\alpha_s=\alpha_{s_0}+\beta_sC+\gamma_sC^2+\delta_sC^3, \quad . \quad . \quad . \quad (53)$$

finally obtained, the coefficients are quite of the same order of magnitude, as regards maximal values, as in the case of one solvate. They are conveniently obtained in terms of a

series of symmetrical expressions of the form

$(M_{s_1}\bar{x}_{s_1}+M_{s_2}\bar{x}_{s_2})$, $(M_{s_1}{}^2\bar{x}_{s_1}+M_{s_2}{}^2\bar{x}_{s_2})$, $(M_{s_1}{}^3\bar{x}_{s_1}+M_{s_2}{}^3\bar{x}_{s_2})$, etc., where $\bar{x}_{s_1}$ and $\bar{x}_{s_2}$ stand for the limiting values $\underset{C\to 0}{\mathrm{Lt}}\, x_{s_1}$ and $\underset{C\to 0}{\mathrm{Lt}}\, x_{s_2}$.

The same procedure exactly, however, can be applied to the more general case (52), but becomes, of course, more complex and laborious as the number of solvates is increased. There can be little doubt that the maximal values of the coefficients remain of the same order of magnitude so long as $G_{x_s}{}''$, etc., are minor quantities as they will be in general; so it will be assumed in what follows that α_s can be expressed in the form (53), and (49) will be used in roughly estimating the ranges of validity of the results we shall obtain.

The Integrated Linear Terms.

We can now evaluate the quantity

$$\int_{c=0}^{\frac{\alpha_s}{m}} d\log(1+\overline{m}C) \quad \text{or} \quad \int_{c=0}^{\alpha_s}(1-a_1C+a_2C^2-a_3C^3)dC,$$

and, subtracting $\log\left(\frac{\overline{m}_0}{\overline{m}}+\overline{m}_0C\right)$ (as evaluated in previous paper), obtain

$$-\log\left(\frac{\overline{m}_0}{\overline{m}}+\overline{m}_0C\right)+\int_{c=0}^{\frac{\alpha_s}{m}} d\log(1+\overline{m}C)$$
$$=e_1C+\tfrac{1}{2}e_2C^2+\tfrac{1}{3}e_3C^3+\tfrac{1}{4}e_4C^4, \quad . \quad (54)$$

where

$$\left.\begin{aligned} e_1&=(\alpha_{s_0}-a_1), & e_3&=(\gamma_s-a_1\beta_s+a_2\alpha_{s_0}-a_3),\\ e_2&=(\beta_s-a_1\alpha_{s_0}+a_2), & e_4&=(\delta_s-a_1\gamma_s+a_2\beta_s-a_3\alpha_{s_0})\end{aligned}\right\}, \quad . \quad (55)$$

and (37) now appears in the more practical form:

$$\left.\begin{aligned}\frac{\partial\psi}{\partial M_0'}&=\phi_M+RC(1-\tfrac{1}{2}a_1C+\tfrac{1}{3}a_2C^2-\tfrac{1}{4}a_3C^3)+G_M\\ \frac{\partial\psi}{\partial n_s}&=\phi_s-R\left[\log c_s+e_1C+\tfrac{1}{2}e_2C^2+\tfrac{1}{3}e_3C^3+\tfrac{1}{4}e_4C^4\right]+G_s\end{aligned}\right\}. \quad (56)$$

Introduction of "Experimental" Concentrations.

We have now to introduce the "experimental" concentrations (c_s', C') in place of the "true" concentrations (c_s, C) in the expressions we have obtained.

Since $$M_0' = M_0 + \Sigma n_s \alpha_s,$$

let us write (as we have already done) N for Σn_s, and also

$$N\bar{\alpha} = \Sigma n_s \alpha_s$$
$$= \Sigma n_s [\alpha_{s_0} + \beta_s C + \gamma_s C^2 + \delta_s C^3],$$

and $$\bar{a} = \bar{\alpha}_0 + \bar{\beta} C + \bar{\gamma} C^2 + \bar{\delta} C^3,$$

so that $$\bar{\alpha}_0 = \frac{\Sigma n_s \alpha_{s_0}}{N}, \quad \bar{\beta} = \frac{\Sigma n_s \beta_s}{N}, \text{ etc.}, \quad . \quad . \quad (56\,a)$$

and $$\frac{c_s}{c_s'} = \frac{C}{C'} = \frac{M_0'}{M_0} = 1 + \bar{\alpha} C$$
$$= 1 + \bar{\alpha}_0 C + \bar{\beta} C^2 + \bar{\gamma} C^3 + \bar{\delta} C^4. \quad . \quad . \quad (57)$$

If $\bar{\alpha}_0$, $\bar{\beta}$, $\bar{\gamma}$, $\bar{\delta}$ are not to be determined, but are already accurately known, equations (56) can be used as they are, for the "experimental" concentrations can be translated into "true" concentrations by means of a curve plotted from (57).

We are dealing now with the more common case where $\bar{\alpha}_0, \bar{\beta}$, etc., are not known.

From (57), in a fairly obvious manner, we obtain

$$\frac{M_0'}{M_0} = 1 + r_1 C' + r_2 C'^2 + r_3 C'^3 + r_4 C'^4, \quad . \quad . \quad (58)$$

where

$$\left.\begin{aligned} r_1 &= \bar{\alpha}_0, & r_3 &= (\bar{\alpha}_0^3 + 3\bar{\alpha}_0\bar{\beta} + \bar{\gamma}), \\ r_2 &= (\bar{\alpha}_0^2 + \bar{\beta}), & r_4 &= (\bar{\alpha}_0^4 + 6\bar{\alpha}_0^2\bar{\beta} + 4\bar{\alpha}_0\bar{\gamma} + 2\bar{\beta}^2 + \bar{\delta}) \end{aligned}\right\}, \quad (59)$$

and

$$\log \frac{M_0'}{M_0} = l_1 C' + l_2 C'^2 + l_3 C'^3 + l_4 C'^4, \quad . \quad . \quad (60)$$

where

$$\left.\begin{aligned} l_1 &= \alpha_0, & l_3 &= (\tfrac{1}{3}\bar{\alpha}_0^3 + 2\bar{\alpha}_0\bar{\beta} + \bar{\gamma}), \\ l_2 &= (\tfrac{1}{2}\bar{\alpha}_0^2 + \bar{\beta}), & l_4 &= (\tfrac{1}{4}\bar{\alpha}_0^4 + 3\bar{\alpha}_0^2\bar{\beta} + 3\bar{\alpha}_0\bar{\gamma} + \tfrac{3}{2}\bar{\beta}^2 + \bar{\delta}) \end{aligned}\right\}. \quad (61)$$

It is now a straightforward matter to eliminate C and c_s from the "linear" terms in (56), obtaining

$$\left.\begin{aligned} \frac{\partial \psi}{\partial M_0'} &= \phi_M + RC'[1 + t_1 C' + t_2 C'^2 + t_3 C'^3 + t_4 C'^4] + G_M, \\ \frac{\partial \psi}{\partial n_s} &= \phi_s - R[\log c_s' + t_1' C' + t_2' C'^2 + t_3' C'^3 + t_4' C'^4] + G_s \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad (62)$$

where

$$\left.\begin{aligned} t_1&=(r_1-\tfrac{1}{2}a_1), & t_3&=[r_3-a_1(r_2+\tfrac{1}{2}r_1^2)+a_2r_1-\tfrac{1}{4}a_3],\\ t_2&=(r_2-a_1r_1+\tfrac{1}{3}a_2), & t_4&=[r_4-a_1(r_3+r_1r_2)+a_2(r_2+r_1^2)-a_3r_1] \end{aligned}\right\}, \quad (63)$$

and

$$\left.\begin{aligned} t_1'&=(e_1+l_1), & t_3'&=[e_1r_2+e_2r_1+\tfrac{1}{3}e_3+l_3],\\ t_2'&=(e_1r_1+\tfrac{1}{2}e_2+l_2), & t_4'&=[e_1r_3+e_2(r_2+\tfrac{1}{2}r_1^2)+e_3r_1+\tfrac{1}{4}e_4+l_4] \end{aligned}\right\}. \quad (64)$$

The Gibbs fundamental relation can readily be applied at this point as a check on the detail.

A Special Procedure, sometimes necessary.

A difficulty arises, however, in the practical application of this result, as it stands, at high concentrations.

We have seen that the series obtained for α_s may be expected, up to sufficiently high concentrations, to "converge practically" in the few terms given, and the same clearly applies to the e-series of (54), (55), and (56).

In passing to "experimental" concentrations, however, we have introduced the r- and l-series for $\dfrac{M_0'}{M_0}$ and $\log\dfrac{M_0'}{M_0}$ respectively, which, when $\bar{\alpha}_0$ and perhaps also $\bar{\beta}$ assume large values, will frequently fail at high concentrations to "converge practically" in so few terms. A glance at the values of the r- and l-coefficients will show this, and also that the difficulty would vanish if $\bar{\alpha}_0$ and $\bar{\beta}$ were small, since $\bar{\gamma}$ and $\bar{\delta}$ occur by themselves only in the first power.

Now since (62) can be used at lower concentrations (with the t and t' series cut down to two terms, see below) to determine $\bar{\alpha}_0$ and $\bar{\beta}$ experimentally, we are at liberty to assume on turning our attention to the higher concentrations that a close estimate of $\bar{\alpha}_0$ and at least a rough estimate of $\bar{\beta}$ can be made, though neither, of course, will be accurate enough for these higher concentrations. Our difficulty can then be overcome by the following procedure.

Let $\bar{\alpha}_0'$, $\bar{\beta}'$, $\bar{\gamma}'$, $\bar{\delta}'$ be estimated values of $\bar{\alpha}_0$, $\bar{\beta}$, $\bar{\gamma}$, $\bar{\delta}$. (The procedure is stated in a general form—if $\bar{\gamma}$ and $\bar{\delta}$ are not estimated $\bar{\gamma}'$ and $\bar{\delta}'$ will be zero.) Then there will be an estimated value (M_0'') of M_0, and "estimated" concentrations (c_s'', C'') referred to it, such that

$$\frac{c_s''}{c_s'}=\frac{C''}{C'}=\frac{M_0'}{M_0''}$$
$$=[1+\bar{\alpha}_0'C''+\bar{\beta}'C''^2+\bar{\gamma}'C''^3+\bar{\delta}'C''^4]. \quad \therefore \quad (65)$$

Comparing this with (57) and the remarks which immediately follow (57), we see that we can easily translate "experimental" into "estimated" concentrations and express our experimental data in terms of the latter, so that it is now only necessary to express (56) in terms of these "estimated" concentrations.

Now $\bar{\alpha}$ being really expressible as some series

$$\bar{\alpha}=\bar{\alpha}_0+\bar{\beta}C+\bar{\gamma}C^2+\bar{\delta}C^3, \quad . \quad . \quad . \quad . \quad (66)$$

of which we do not know the coefficients accurately, let this be equivalent to some series

$$\bar{\alpha}=\bar{\alpha}_0+\bar{\beta}C''+\bar{\gamma}''C''^2+\bar{\delta}''C''^3. \quad . \quad . \quad . \quad (67)$$

Then

$$M_0=M_0'-N(\bar{\alpha}_0+\bar{\beta}C''+\bar{\gamma}''C''^2+\bar{\delta}''C''^3). \quad . \quad (68)$$

But from (65)

$$M_0''=M_0'-N(\bar{\alpha}_0'+\bar{\beta}'C''+\bar{\gamma}'C''^2+\bar{\delta}'C''^3), \quad . \quad (69)$$

so that

$$M_0=M_0''-N[(\Delta\alpha)+(\Delta\beta)C''+(\Delta\gamma')C''^2+(\Delta\delta')C''^3], \quad (70)$$

where

$$(\Delta\alpha)=(\bar{\alpha}_0-\bar{\alpha}_0'), \qquad (\Delta\gamma')=(\bar{\gamma}''-\bar{\gamma}'), \text{ etc.} \quad . \quad (71)$$

And then we have

$$\frac{c_s''}{c_s}=\frac{C''}{C}=\frac{M_0}{M_0''}=1-[(\Delta\alpha)C''+(\Delta\beta)C''^2 + (\Delta\gamma')C''^3+(\Delta\delta')C''^4], \quad . \quad (72)$$

which can readily be shown to be equivalent to

$$\frac{c_s}{c_s''}=\frac{C}{C''}=\frac{M_0''}{M_0}=1+(\Delta\alpha)C+(\Delta\beta)C^2+(\Delta\gamma)C^3+(\Delta\delta)C^4, \quad . \quad . \quad . \quad (73)$$

where

$$(\Delta\gamma')=[(\Delta\gamma)+(\Delta\alpha)(\Delta\beta)];$$
$$(\Delta\delta')=[(\Delta\delta)+2(\Delta\alpha)(\Delta\gamma)+(\Delta\beta)^2+(\Delta\alpha)^2(\Delta\beta)]. \quad (74)$$

On comparing this with (57), it is at once obvious that the result of introducing (c_s'', C'') the "estimated" concentrations into (56) can be written down at once from equations (58) to (64) by simply writing c_s'', C'' in place of c_s' and C' respectively, and $(\Delta\alpha)$, $(\Delta\beta)$, $(\Delta\gamma)$, $(\Delta\delta)$ in place of $\bar{\alpha}_0$, $\bar{\beta}$, $\bar{\gamma}$, and $\bar{\delta}$ respectively.

$(\Delta\beta)$ being small, and $(\Delta\alpha)$ very small, it is clear that the new t and t' series will converge with the necessary rapidity.

Comparison with experimental data expressed in "estimated" concentrations will thus give $(\Delta\alpha)$, $(\Delta\beta)$, $(\Delta\gamma)$, and $(\Delta\delta)$, and hence also $(\Delta\gamma')$ and $(\Delta\delta')$ [from (74)]. This will give $\bar{\alpha}_0$, $\bar{\beta}$, $\bar{\gamma}''$, and $\bar{\delta}''$, and we can then at once get $\bar{\gamma}$ and $\bar{\delta}$, for it is easily shown that

$$\left.\begin{aligned}\bar{\gamma}'' &= \{\bar{\gamma}+\bar{\beta}(\Delta\alpha)\}\,;\\ \bar{\delta}'' &= \{\bar{\delta}+2\bar{\gamma}(\Delta\alpha)+\bar{\beta}[(\Delta\beta)^2+(\Delta\alpha)^2]\}.\end{aligned}\right\} \quad . \quad . \quad (75)$$

This procedure being available when $\bar{\alpha}_0$ and $\bar{\beta}$ are large, the highest concentrations, for which four-term expansions of $\bar{\alpha}$ and $\bar{\alpha}_s$ suffice, fall within the scope of the results given here and it has been seen that these concentrations are high.

In considering (62) in the sequel, it is understood that this special procedure will be resorted to where necessary, in which case $(\Delta\alpha)$ etc. will replace $\bar{\alpha}_0$ etc. in the coefficients t_1, t_1', etc.

Main Result of the Analysis.

Having now completed the analysis we may conveniently use M_0, C, c_s, in place of M_0', C', c_s', for the "experimental" quantities, since the corresponding "true" quantities will but seldom have to be considered.

If, then, we write

$$\left.\begin{aligned}J_M &= RC^2(t_1+t_2C+t_3C^2+t_4C^3)\\ -J_s &= RC(t_1'+t_2'C+t_3'C^2+t_4'C^3)\end{aligned}\right\}, \quad . \quad . \quad (76)$$

(62) takes the form

$$\left.\begin{aligned}\frac{\partial\psi}{\partial M_0} &= \phi_M+RC+J_M+G_M\\ \frac{\partial\psi}{\partial n_s} &= \phi_s-R\log c_s+J_s+G_s\end{aligned}\right\}, \quad . \quad . \quad . \quad (77)$$

and, in fact, if, corresponding to G, we write

$$\phi=\phi_M+\Sigma c_s\phi_s, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (78)$$

$$J=J_M+\Sigma c_sJ_s, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (79)$$

$$=-RC^2(t_1+\tfrac{1}{2}t_2C+\tfrac{1}{3}t_3C^2+\tfrac{1}{4}t_4C^3), \quad . \quad . \quad (80)$$

(77) can be condensed to

$$\frac{\psi}{M_0}=\phi+R\Sigma c_s(1-\log c_s)+J+G, \quad . \quad . \quad (81)$$

which is perhaps the simplest and most concise expression of the main result of the analysis of this and the preceding papers.

PRACTICAL SIGNIFICANCE AND APPLICATION.

Now the equation

$$\frac{\psi}{M_0} = \phi + R\Sigma c_s(1 - \log c_s), \quad . \quad . \quad . \quad (82)$$

or less concisely, but more practically,

$$\left.\begin{aligned} \frac{\partial \psi}{\partial M_0} &= \phi_M + RC \\ \frac{\partial \psi}{\partial n_s} &= \phi_s - R \log c_s \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (83)$$

is equivalent to the Raoult-van't Hoff limiting laws of dilute solution, the older criterion of "perfect" behaviour.

In the circumstances considered in this paper (as stated at the beginning) C and c_s are "experimental"—that is, directly determinable—quantities, and to the experimenter, as such, J and G will appear together simply as the measurable departure (J + G) from "perfect" behaviour according to the older (van't Hoff) criterion.

In fact, in terms of the "activity coefficient" (γ) of G. N. Lewis, and the osmotic coefficient ($1 - \varphi$) of Brönsted, expressions now much used in practice for the observed departures from (van't Hoff's) "perfect" behaviour, we have

$$\left.\begin{aligned} \log \gamma &= -\frac{1}{R}(J_s + G_s) \\ \bar{\varphi} - 1 &= \frac{1}{RC}(J_M + G_M) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (84)$$

where $\bar{\varphi}$ is a *mean* quantity for the whole solution, characteristic, therefore, of the given solutes, *mixed in given proportions.*

It may be convenient therefore to call (J + G) the "apparent" general terms, G the "true" general terms, and J the "pseudo-general" terms. It is, of course, only G which represents real departure from perfect behaviour (as defined by the linearity of the full "molecular" expression for ψ; see second paper, Section II.).

It is clear that any physical interpretation of the "apparent" general terms based upon the ignoring of either J or G, without due consideration and adequate grounds, must be unsound, and that in general neither will be negligible, so that a separation of J from G must be attempted.

This will only be possible by a critical application of the

limitations imposed upon J and G by their respective physical significances.

It seems reasonable, however, that when all possible has been done in this direction, if doubt still remains as to whether all or some portion of the observed effects should be assigned to J or to G, a "casting-vote" should be given (temporarily) in favour of J, since J does not represent real departure from perfect behaviour, properly defined.

It is possible that G may be completely determined on theoretical grounds alone in certain cases, the nearest approach to this, so far, being in the case of electrolytes, or rather of a mixture of ions all of the same valency, for which the (probable) *form* and *order of magnitude* of G, in (sufficiently) dilute solution, was obtained in the first of these papers, on the basis of a calculation of Milner's.

With regard to J, besides the fact that it takes the form of a series of ascending integral powers of C, the *total* solute concentration, a good deal can be deduced from the form of the coefficients t_1', t_1, etc., and the physical significance of the three series of quantities, the "solvent-constants" (a_1, a_2, a_3), the α-series ($\bar{\alpha}_0$, $\bar{\beta}$, $\bar{\gamma}$, $\bar{\delta}$), and the α_s-series (α_s, β_s, γ_s, δ_s).

The Form of the Coefficients t_1, t_1', etc.

(59), (61), (63), (64) give us these coefficients as functions, at first sight rather complex, of these three series of quantities, but for practical purposes this complexity is only apparent, for each successive term of the J_s-series introduces just one further term from each of the three series of physically significant quantities, and introduces it in the first degree, while in J_M the same is the case except that the α_s-series does not enter.

These coefficients can be obtained in a much simpler and more practical form by introducing the quantities t_s, h_s, k_s, ..., and the corresponding mean quantities $\bar{t}$, $\bar{h}$, $\bar{k}$, ..., such that

$$\left.\begin{aligned} t_s-\alpha_{s_0} &= t-\bar{\alpha}_0 = -\tfrac{1}{2}a_1 \\ h_s-\beta_s &= \bar{h}-\bar{\beta} = \tfrac{1}{3}a_2-\tfrac{1}{4}a_1^2 \approx 1\tfrac{1}{2}a_1^2 \\ k_s-\gamma_s-\tfrac{1}{2}a_1h_s &= \bar{k}-\bar{\gamma}-\tfrac{1}{2}a_1\bar{h} \\ &= -\tfrac{1}{4}a_3+\tfrac{1}{3}a_1a_2-\tfrac{1}{8}a_1^3 \approx -2\tfrac{1}{4}a_1^3 \end{aligned}\right\}, \quad (85)$$

and so on, for we then obtain

$$\left.\begin{array}{ll} t_1=\bar{t}\,; & t_1'=t+\bar{t}_s \\ t_2=\bar{t}^2+h\,; & t_2'=(\bar{t}t_s+\frac{1}{2}\bar{t}^2)+(\bar{h}+\frac{1}{2}h_s) \\ t_3=\bar{t}^3+3\bar{t}\bar{h}+\bar{k}\,; & t_3'=(\bar{t}^2t_s+\frac{1}{3}\bar{t}^3)+(2\bar{t}\bar{h}+t_s\bar{h}+\bar{t}h_s) \\ & \quad +(\bar{k}+\frac{1}{3}k_s) \end{array}\right\}, \quad (86)$$

and so on.

Clearly the coefficients of J_M alone, determined term by term (with increasing concentration) will yield the quantities t, $\bar{h}$, etc., one by one, while, if the coefficients of both J_M and J_s are determined, the pairs (t_1, t_1'), (t_2, t_2'), etc., will yield in succession the pairs of quantities $(\bar{t}, t_s)$, (h, h_s), etc.

It must be observed, however, that while t_s, h_s, etc., are *constants* peculiar to the solute s (in a given solvent), on the other hand, $\bar{t}$, $\bar{h}$, etc., are the corresponding *average* quantities for the whole solution, and so depend upon the *relative proportion in which these solutes are present* [see (56 *a*)]. Some cases where $\bar{t}$, $\bar{h}$, etc., vary under the conditions of experiment can in fact be dealt with, without difficulty, as will be shown later, but, of course, it is simpler if they are constant.

Two important cases where this is so present themselves, viz., the case where there is only one solute and the case where there are two, but the concentration of the one is negligible in comparison with that of the "second," the *former* being the solute s. These two cases gain further importance from the fact that the form of G, the "true" general terms, will here probably be simplest, depending in the second case almost entirely on the "second" solute.

The last point suggests, however, that in the matter of separating J from G, cases where $\bar{t}$, $\bar{h}$, etc., vary under the conditions of experiment may prove more useful.

The Quantities α_{s_0}, $\bar{\alpha}_0$, a_1, etc.

(85) shows that the evaluation of $\bar{t}$, t_s, etc., would not give us these quantities (in general), but since the differences shown in (85) will generally be much smaller than the (corresponding) quantities $\bar{\alpha}_0$, $\bar{\alpha}_{s_0}$, etc., a rough estimate of these differences (all fairly nearly expressible in terms of a_1, which is something slightly greater than the mean molecular weight of the pure solvent) will suffice to determine $\bar{\alpha}_0$, $\bar{\alpha}_{s_0}$, etc., with a *relative* error much less than that of the estimate.

Actually, to determine the solvent constants experimentally

(and so permit accurate evaluation of $\bar{\alpha}_{s_0}$, $\bar{\alpha}_0$, etc.) we shall require an *entirely unsolvated solute* (such as an inert gas in water), for which t_s will be $(-\frac{1}{2}a_1)$, and so on *.

That only the solute s need be unsolvated is an important point, since the solubility of the more inert gases (for instance) is small.

Physical Significance and Limitations of the Quantities.

The quantities $\bar{\alpha}_0$, α_{s_0}, β_s, etc., though more difficult to estimate than the solvent-constants, are not, of course, merely arbitrary parameters by any means

(49), for instance, shows that if only one solvate is formed by the solute s, then

$$\left(\alpha_{s_0} - \frac{\beta_s}{\alpha_{s_0}}\right) = M_s, \quad . \quad . \quad . \quad . \quad . \quad (87)$$

so that the composition of the solvate is determinable from α_{s_0} and β_s, and, of course, M_s will have to be an integral number of times the molecular weight of the solvent. Similarly, if two solvates are formed and the amount of (s) remaining unsolvated is very small, then, on the assumption of perfect solution α_{s_0}, β_s, and γ_s will suffice to determine the composition of *both* solvates, according to the analysis mentioned, but not inserted, above. If the unsolvated residue is not negligible, δ_s will be required.

A more general limitation is that so long as only "positive" solvation is in question (see first pages of this paper) α_{s_0} cannot be negative, and β_s *cannot be positive*, the latter being demonstrable from "Le Chatelier's Principle."

In other words, t_s may be a fairly large positive quantity, but only a quite small negative quantity, ranging, in fact, from $-\frac{1}{2}a_1$ to the highest probable value for M_s. Similarly, h_s can range from (very nearly) $\frac{1}{2}a_1^2$ to the highest probable value for $\frac{1}{4}M_s^2$. When the solvent is water a_1 may be 60, possibly even higher near 0° C., and M_s might easily be 180 (decahydrate), while, of course, hydrates much higher than this are known even in the solid state with low aqueous vapour-pressure, so that a value of M_s as high as 300 would not be improbable in certain cases.

* Compare here 2nd paper *loc. cit.*, p. 241.

Ranges of Applicability of Approximations.

Our four-term expansion of α_s leads to (62) or (76) or (80) which may be called a "fifth-approximation" and from which, by curtailing the series one term at a time, the fourth, third, second, and first approximations are obtained.

Owing to the diversity of possible magnitudes of the quantities α_{s_0}, $\bar{\alpha}_0$, β_s, etc., precise statement of the ranges of applicability of these successive approximations is not possible, particularly in the case of the higher ones, but some indication of probable range of the lower, for aqueous solution, may be given.

The third (as far as t_2) will commonly suffice as far as Molar (M.) or 2M. solution (but will often go further), the second (as far as t_1) probably up to $\frac{1}{2}$M. or M. (sometimes further), while the first in which the pseudo-general terms J are omitted altogether *cannot be assumed to be accurate to* 0·2 *per cent. above hundredth-molar* $\left(\frac{\mathrm{M}}{100}\right)$ concentration. When hydrates higher than the decahydrate are not improbable, the upper limit for the first approximation must be set still lower.

Examples of Application.

Detailed application of the results of these papers to existing data must be postponed, but it may be of interest to cite one or two of the simpler instances. Consider, first, a perfect solution (G vanishing) of middle concentration, for which our "second approximation" will suffice, so that

$$\frac{\partial \psi}{\partial \mathrm{M}_0} = \phi_{\mathrm{M}} + \mathrm{RC}[1 + t_1\mathrm{C}]. \quad . \quad . \quad . \quad . \quad (88)$$

If P be the osmotic pressure, defined and measured so that the pressure on the pure solvent is relatively negligible, and β the coefficient of compressibility of the pure solvent, then writing (with van't Hoff) V_0 for $\frac{1}{\rho_0\mathrm{C}}$, and considering the smallness of $t_1\mathrm{C}$ relative to unity, we easily obtain

$$\mathrm{P}\left[\mathrm{V}_0 - \left(\frac{t_1}{\rho_0} + \frac{1}{2}\beta\mathrm{RT}\right)\right] = \mathrm{RT}, \quad . \quad . \quad . \quad (89)$$

where, if we can neglect the effect of the pressures used on the solvation of the solute, the quantity in round brackets is a constant at constant temperature.

Since, further, at these middle concentrations the density of the solution is expressible as a linear function of the concentration, so that the "partial-molal volume" v of the solute is a constant (at constant temperature),

$$V = V_0 + v, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (90)$$

where V is the volume of *solution* containing one gm.-molecule of solute, and (89) can take the form

$$P[V - b] = RT, \quad . \quad . \quad . \quad . \quad . \quad . \quad (91)$$

where b is constant at constant temperature, and

$$b = \left[v + \frac{t_1}{\rho_0} + \frac{1}{2}\beta RT \right]. \quad . \quad . \quad . \quad . \quad . \quad (92)$$

Equation (91) was put forward by O. Sackur *, in analogy with van der Waal's equation for imperfect gases, and was shown to represent the data for middle concentrations. We see that for a perfect solute this equation can be predicted for such concentrations.

Now consider a slightly soluble solute s in a solution containing also a "second" solute in concentration C, relative to which c_s is negligible.

If G_s is negligible, we have

$$\frac{\partial \psi}{\partial n_s} = \phi_s - R \log c_s + J_s. \quad . \quad . \quad . \quad . \quad . \quad (93)$$

In solubility measurement we have the solution in equilibrium with a phase consisting entirely of the solute s at constant temperature and pressure, so that

$$\log c_s - \frac{1}{R} J_s (= \log c_s \gamma_s) = \text{constant}, \quad . \quad . \quad (94)$$

where c_s is the solubility in presence of the concentration C of the "second" solute. If c_{s_0} be the solubility in absence of a "second" solute, we have

$$\log c_{s_0} = \log c_s - \frac{1}{R} J_s, \quad . \quad . \quad . \quad . \quad . \quad . \quad (95)$$

or

$$\log \frac{c_{s_0}}{c_s} (= \log \gamma_s) = -\frac{1}{R} J_s. \quad . \quad . \quad . \quad . \quad (96)$$

For concentrations at which the "second approximation" suffices, we expect then to find

$$\log \frac{c_{s_0}}{c_s} = t_1' C = (\bar{t} + t_s) C, \quad . \quad . \quad . \quad . \quad (97)$$

where t_1' is a constant, since $\bar{t}$ depends practically entirely

* *Zeitschr. f. Phys. Chem.* (1910).

on the "second" solute. We thus obtain a simple first-approximation law for the *solubility lowering* of a slightly soluble perfect solute produced by the addition of other solutes.

If the "second" solute be an electrolyte G_M will not vanish, but since at the very moderate concentrations to which (97) would apply, G will probably be practically entirely due to the electrostatic forces between the ions, G_s may be expected to vanish if (*s*) is a non-electrolyte. Thus (97) may be expected to apply to the solubility lowering of slightly soluble non-electrolytes—the more inert gases, for instance—produced by the addition of small quantities of salts, providing the *complete ionization* theory is accepted. (97) therefore constitutes a prediction, compatible with perfect behaviour on the part of the non-electrolyte of the *empirical law of Setchenow*, which latter should, however, be re-written in terms of solvent-weight (instead of solution-volume) concentrations.

For binary electrolytes we see that 1000C (roughly) equals the equivalent or twice the equivalent concentration according as the ions are bivalent or univalent respectively, and that

$$2t_1' = (t_c + t_a + 2t_s), \quad . \quad . \quad . \quad . \quad . \quad (98)$$

where t_c is peculiar to the cation, t_a to the anion, and t_s to the slightly soluble non-electrolyte.

The data tabulated by Rothmund seem on investigation to be of somewhat doubtful accuracy, and the concentrations examined too high. Moreover, they are expressed (as percentages) in terms of Setchenow's law, that is, in terms of solution-volume concentrations, and the recalculation is thus necessary.

They serve at once, however, to show that our prediction is quantitatively quite of the right order of magnitude to suffice. In particular, the smallness of the few negative values should be observed.

Among the more reliable figures there is also some evidence of the parallelisms which the additive form of (98) would predict for the recalculated values, while the greater degree of solvation clearly assigned to the ions of higher valency, (Mg^{++}, SO_4^{--}, CO_3^{--}), is quite what we should expect. Closer examination and more accurate measurement will be necessary to determine how far and for what range of concentration G_s can be neglected here.

Finally, the single case (as yet) of (probably) accurately known "true" general terms may be introduced.

It was shown in the first of these papers that in the case of a mixture of ions, all of the same valency, theory alone is able to predict, for (sufficiently) dilute solution, a simple limiting form

$$G = -R\phi' C_i^{3/2}, \quad . \quad . \quad . \quad . \quad . \quad (99)$$

where $2C_i$ is the total ion-concentration *. The range of validity of the "point-charge" assumption, on which this form depends, should be greatest in the case of the univalent ions of simple structure, and might here extend to, or even above, tenth-normal concentration.

Assuming this, and supposing that, while other solutes (typified by s) besides the ions (typified by j) are present, there are no other "true" general terms at these low concentrations, we have

$$\frac{\psi}{M_0} = \phi + R[C - \Sigma c_s \log c_s - \Sigma c_j \log c_j] + J - R\phi' C_i^{3/2}, \quad (100)$$

or

$$\left.\begin{aligned} \bar{\varphi} - 1 &= \frac{1}{RC} J_M + \tfrac{1}{2}\phi' \frac{C_i^{3/2}}{C}, \\ \log \gamma_s &= -\frac{1}{R} J_s, \\ \log \gamma_j &= -\frac{1}{R} J_j + \tfrac{3}{4}\phi' C_i^{1/2} \end{aligned}\right\}, \quad . \quad . \quad . \quad (101)$$

where Σc_j is $2C_i$, and C is $\Sigma c_s + \Sigma c_j$.

At the concentrations considered, J_j of course, reduces to one term, and we have

$$\left.\begin{aligned} \bar{\varphi} - 1 &= \bar{t} C + \tfrac{1}{2}\phi' \frac{C_i^{3/2}}{C}, \\ \log \gamma_s &= (\bar{t} + t_s) C, \\ \log \gamma_j &= (\bar{t} + t_j) C + \tfrac{3}{4}\phi' C_i^{1/2}, \end{aligned}\right\} \quad . \quad . \quad . \quad (102)$$

In practice, $\log \gamma_j$ will always be a mean quantity for the two ions of the electrolyte j separated, so that

$$\log \gamma_j \left(= \tfrac{1}{2} \log \gamma_{jc} \cdot \gamma_{ja}\right) = (\bar{t} + \tfrac{1}{2} t_{jc} + \tfrac{1}{2} t_{ja}) C + \tfrac{3}{4}\phi' C_i^{1/2}, \quad (103)$$

where t_{jc} and t_{ja} are peculiar to cation and anion respectively.

For a single binary electrolyte by itself

$$\left.\begin{aligned} \log \gamma_j &= 2(t_{jc} + t_{ja}) C_i + \tfrac{3}{4}\phi' C_i^{1/2}, \\ \varphi - 1 &= 2(t_{jc} + t_{ja}) C_i + \tfrac{1}{2}\phi' C_i^{1/2} \end{aligned}\right\}, \quad . \quad . \quad (104)$$

* See equations (88), (89), (92) of 1st paper.

C_i being $2c_i$. Now t_{jc} and t_{ja}, being constants peculiar to the particular ions constituting the electrolyte, it is plain that we have here a possible explanation of the *specific divergences of the simple uni-uni-valent electrolytes* at and below (say) tenth-normal concentration, *not involving the rejection of the "point-charge" assumption* at these concentrations.

As might be expected, the limiting "law" $bc^{1\cdot2}$ for ϕ or $\log\gamma$, found by G. N. Lewis to apply, below (about) hundredth normal solution, to uni-uni-valent electrolytes, can be extended to cover the data to higher concentrations in the form $(bc^{1\cdot2}+ac)$, where a, unlike b, is specific, or peculiar, to the particular electrolyte. But, further, the values of a required are quite of the order of magnitude to accord with the interpretation of (104).

One other particular case of (103) may be cited, viz. the case of two electrolytes together, the concentration of the one, j, being negligible compared with that of the other, i, so that C_i is practically $2c_i$, and $\bar{t}$ depending on i only can be written $(\frac{1}{2}t_{ic}+\frac{1}{2}t_{ia})$, whence

$$\log\gamma_j = (t_{jc}+t_{ja}+t_{ic}+t_{ia})C_i+\tfrac{3}{4}\phi' C_i^{1/2}, \quad . \quad (105)$$

in which, it is seen, the specific properties (as regards solvation) of the *four ions* present enter very simply, symmetrically and additively.

These few brief and very limited illustrations must suffice for the present rather lengthy paper.

Appendix I.—The Expansions of U and V.

As in the previous treatment of "complex solvents" the full consideration of the expansions of U and V, the total energy and volume of the solution, is postponed, but one point concerning the simple linear forms applying to "perfect solution" is briefly considered.

We have then the "molecular" expressions

$$\left.\begin{aligned} U &= \Sigma n_{0_1}u_{0_1}+\Sigma n_s[(1-X_s)u_{s_0}+\Sigma x_{s_1}u_{s_1}],\\ V &= \Sigma n_{0_1}v_{0_1}+\Sigma n_s[(1-X_s)v_{s_0}+\Sigma x_{s_1}v_{s_1}],\\ Q &= \Sigma n_{0_1}q_{0_1}+\Sigma n_s[(1-X_s)q_{s_0}+\Sigma x_{s_1}q_{s_1}] \end{aligned}\right\}, \quad . \quad (106)$$

and, starting from the results of the previous paper, we have

$$\begin{aligned} U &= M_0u_M+\Sigma u_{0_1}\Delta n_{0_1}+\Sigma n_s[(1-X_s)u_{s_0}+\Sigma x_{s_1}u_{s_1}]\\ &= M_0'u_M+\Sigma u_{0_1}\Delta n_{0_1}+\Sigma n_s[(1-X_s)u_{s_0}+\Sigma x_{s_1}u_{s_1}-\alpha_s u_M]. \end{aligned}$$

Writing

$$\operatorname*{Lt}_{C\to 0}\left[(1-X_s)u_{s_0}+\Sigma x_{s_1}u_{s_1}-\alpha_s u_M\right]=u_s, \quad . \quad (107)$$

and, of course,

$$\Delta x_{s_1}=\int_{C=0}^{} dx_{s_1},$$

we have

$$U=M_0'u_M+\Sigma n_s u_s+\{\Sigma u_{0_1}\Delta n_{0_1}+\Sigma n_s\Sigma(u_{s_1}-u_{s_0}-M_{s_1}u_M)\Delta x_{s_1}\}, \quad . \quad . \quad . \quad (108)$$

and, similarly,

$$V=M_0'v_M+\Sigma n_s v_s+\{\Sigma v_{0_1}\Delta n_{0_1}+\Sigma n_s\Sigma(v_{s_1}-v_{s_0}-M_{s_1}v_M)\Delta x_{s_1}\}, \quad . \quad . \quad . \quad (109)$$

$$Q=M_0'q_M+\Sigma n_s q_s+\{\Sigma q_{0_1}\Delta n_{0_1}+\Sigma n_s\Sigma(q_{s_1}-q_{s_0}-M_{s_1}q_M)\Delta x_{s_1}\}, \quad . \quad . \quad . \quad (110)$$

It is plain (*cf.* simple demonstration in previous paper) that the bracketed quantity in (110) is the heat developed on "infinite" dilution of the solution, and it also clearly represents the heat of the chemical action involved in the change of the free solvent and of the solvation equilibria to their limiting states pertaining to "infinite" dilution. When only one solute, (*s*), is present, this heat of dilution assumes the simple form—per gm. molecule of solute—

$$\left[\frac{1}{n_s}\Sigma q_{0_1}\Delta n_{0_1}+\Sigma(q_{s_1}-q_{s_0}-M_{s_1}q_M)\Delta x_{s_1}\right]. \quad . \quad (111)$$

Similarly, the bracketed quantity in (109) is the "contraction of dilution."

We saw in the previous paper that

$$\left.\begin{aligned} u_M &= T^2\frac{\partial}{\partial T}\phi_M, \\ v_M &= -T\frac{\partial}{\partial p}\phi_M \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (112)$$

The demonstration that

$$\left.\begin{aligned} u_s &= T^2\frac{\partial}{\partial T}\phi_s, \\ v_s &= -T\frac{\partial}{\partial p}\phi_s \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (113)$$

is not quite so obvious, but will be obtained without difficulty if (13), (10), (6), and (3) are used in the order named.

Finally, we have the interesting relations

$$\left.\begin{aligned} T^2\frac{\partial J}{\partial T} &= \{\Sigma u_{0_1}\Delta c_{0_1}' + \Sigma c_s'\Sigma(u_{s_1} - u_{s_0} - M_{s_1}u_M)\Delta x_{s_1}\}, \\ -T\frac{\partial J}{\partial p} &= \{\Sigma v_{0_1}\Delta c_{0_1}' + \Sigma c_s'\Sigma(v_{s_1} - v_{s_0} - M_{s_1}v_M)\Delta x_{s_1}\} \end{aligned}\right\}. \quad (114)$$

Appendix II.

The practical significance of (39) may be illustrated in a simple way, by means of a suppositious case in connexion with strong electrolytes, entirely analogous to that given in the appendix to the previous (second) paper.

The "general terms" for a dilute solution of a binary strong electrolyte being

$$M_0'G'' = RM_0'\phi' c_s'^{3/2}, \quad . \quad . \quad . \quad . \quad (115)$$

we suppose that the "effective" dielectric constant (D) depends on c_s' in such a way that ϕ' is a linear function of c_s',

$$\phi' = \phi_0'(1 + \alpha c_s'). \quad . \quad . \quad . \quad . \quad . \quad (116)$$

If this effect of c_s' on D is independent of its effect on the solvation-equilibria, then we have

$$\Sigma\frac{\partial G''}{\partial x_{s_1}}dx_{s_1} = 0,$$

so that

$$\left.\begin{aligned} G = G'' &= R\phi' c_s'^{3/2} = R\phi_0' c_s'^{3/2}(1 + \alpha c_s'), \\ G_s = G_s'' &= \tfrac{3}{2}R\phi' c_s'^{1/2} = \tfrac{3}{2}R\phi_0' c_s'^{1/2}(1 + \alpha c_s'), \\ G_M = G_M'' &= -\tfrac{1}{2}R\phi' c_s'^{3/2} = -\tfrac{1}{2}R\phi_0' c_s'^{3/2}(1 + \alpha c_s') \end{aligned}\right\}. \quad (117)$$

If, on the other hand, the effect of c_s' on D is entirely dependent on its effect on the solvation-equilibrium, then

$$\begin{aligned} \Sigma\frac{\partial G''}{\partial x_{s_1}}\frac{dx_{s_1}}{dc_s'} &= Rc_s'^{3/2}\frac{\partial \phi'}{\partial c_s'} \\ &= R\alpha\phi_0' c_s'^{3/2} \end{aligned}$$

and

$$\int_{C=0}\frac{1}{c_s'}\Sigma\frac{\partial G''}{\partial x_{s_1}}dx_{s_1}=\int_{C=0}\frac{1}{c_s'}\Sigma\frac{\partial G''}{\partial x_{s_1}}\frac{dx_{s_1}}{dc_s'}dc_s'$$
$$=\tfrac{2}{3}R\alpha\phi_0'c_s'^{\,3/2},$$

so that

$$\left.\begin{aligned}G &= G'' - c_s'\int_{C=0}\frac{1}{c_s'}\Sigma\frac{\partial G''}{\partial x_{s_1}}dx_{s_1}=R\phi_0'c_s'^{\,3/2}(1+\tfrac{1}{3}\alpha c_s')\\ G_s &= G_s'' - \int_{C=0}\frac{1}{c_s'}\Sigma\frac{\partial G''}{\partial x_{s_1}}dx_{s_1}=\tfrac{3}{2}R\phi_0'c_s'^{\,1/2}(1+\tfrac{5}{3}\alpha c_s')\\ G_M &= G_M'' = -\tfrac{1}{2}R\phi_0'c_s'^{\,3/2}(1+\alpha c_s')\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (118)$$

As in the previous paper, it is to be remarked that in such a case, if D were the ordinary measurable or "bulk" dielectric constant, the necessary modification of the general terms (if not negligible) might be introduced without knowledge of the *way* in which the degree of solvation of the solute was able to affect D.

In both cases also it may be observed that something might be learned by the introduction of other solutes, since both the constitution of the solvent and degree of solvation depend mainly, if not entirely, on the total concentration (C—not on the concentration c_s' of the solute (electrolyte) considered.

The case of electrolytes provides an interesting and important example of the (probable) fulfilment of the condition for the vanishing of (40), though the solution is not perfect.

It seems quite likely that—at least in the more dilute solutions—the ions will behave essentially and approximately as point-charges, whether solvated or not.

The general terms for a solution of ions obtained in the last section of the first of these papers would then hold equally for solvated and unsolvated ions. That is, we should have

$$G_{s_0}'=G_{s_1}'=G_{s_2}'=\ldots,$$

and since M_1G_M' will be a much smaller quantity in dilute solution, $G_{x_{s_1}}''$, etc., will probably be quite small.

For $G_{x_{s_1}}''$, etc., to vanish altogether, we should require that the "bound" or "absorbed" solvent should continue to function in the same way as the free solvent, as separating dielectric between the point-charges.

Appendix III.

The form of the coefficients in (86) suggests an alternative method of meeting the practical difficulty of slow convergence of the J series, which will be preferable in many cases though not always) to that already given on account of its very attractive simplicity—both formal and practical.

Extending (85) to the fourth term

$$(l_s-\delta_s-a_1k_s+\tfrac{1}{3}a_2h_s)=(\bar{l}-\bar{\delta}-a_1\bar{k}+\tfrac{1}{3}a_2\bar{h})$$
$$=(-\tfrac{1}{16}a_1^4+\tfrac{1}{4}a_1^2a_2-\tfrac{1}{4}a_1a_3-\tfrac{1}{9}a_2^2+\tfrac{1}{5}a_4)\approx\tfrac{1}{38}a_1^4, \quad . \quad (119)$$

we have for the coefficients of the J_M-series,

$$\left.\begin{array}{ll} t_1=\bar{t}\,; & t_3=(\bar{t}^3+3\bar{t}\,\bar{h}+\bar{k}) \\ t_2=(\bar{t}^2+\bar{h}); & t_4=(\bar{t}^4+6\bar{t}^2\bar{h}+2\bar{h}^2+4\bar{t}\,\bar{k}+\bar{l}) \end{array}\right\}, \quad (120)$$

and on comparing this with (59) it is at once seen that if we write C′ for $\left(C+\frac{1}{R}J_M\right)$, then

$$\frac{1}{RC}J_M=\left(\frac{C'}{C}-1\right)=\bar{t}C'+\bar{h}C'^2+\bar{k}C'^3+\bar{l}C'^4. \quad . \quad (121)$$

Also (but less obviously), if

$$\frac{c_s'}{c_s}=\frac{C'}{C},$$

we find

$$R\log c_s-J_s=R\log c_s'-J_s', \quad . \quad . \quad . \quad (122)$$

where

$$-J_s'=RC'(t_s+h_sC'+K_sC'^2+l_sC'^3). \quad . \quad . \quad (123)$$

These "concentrations" (c_s', C′) have no simple physical significance, though they will approximate roughly to the "true" concentrations of the earlier analysis. They are, however, a great practical convenience, since the series in (121) and (123) will clearly converge "practically" in few terms so long as the expansions of α_s and $\bar{\alpha}$ (in ascending integral powers of the total "true" concentration) do so, that is, as we have seen, up to very high concentrations.

Now, supposing either that we can neglect G (thus making, tentatively, the assumption of perfect solution), or that we can separate G from J in our measurements, then solvent-separation data will give us J_M and solute-separation

data will determine (differences in) $R \log c_s - J_s$, that is, $R \log c_s' - J_s'$. In the former, therefore, $\frac{C'}{C}$ as well as C' is a measured quantity, and when obtained (graphically) as a series of integral powers of C' gives the quantities $\bar{t}$, $\bar{h}$, ..., directly.

But without (and independently of the precision of) this determination of $\bar{t}$, $\bar{h}$, ..., the measurement of $\frac{C'}{C}$ makes c_s' a measured quantity, so that a combination of solvent-separation data and solute-separation data gives us J_s' directly as a measured quantity, and this when obtained (graphically) as a series of integral powers of C' gives us t_s, h_s, ..., referring to the solute "separated," at once.

It is, of course, in the obtaining of the series to express, as accurately as possible, the data, that the *essential* advantage, the rapid convergency, attained by the use of the "convenience-concentrations" (c_s', C'), appears. The simplification, however, of the coefficients of the series (as compared with (62)) will probably mean greater accuracy in the evaluation of $\bar{t}$, $\bar{h}$, ..., t_s, h_s, ...

Summary of Papers II. and III.

Paper II., *Section* I. A postulate, a rider to the definition of "a molecule," is proposed as the basis of rigorous molecular thermodynamics, and its significance is discussed.

Section II. The theoretical basis of the method and the nature of the general problem are outlined.

Section III. Analysis of the problem of "complex solvents."

Paper III. (the present) contains some analysis of the problem of "solvation of solutes," to which is attached a discussion of the results with some brief preliminary illustrations.

Balliol College,
March 1922.

LVI. *The Law of Distribution of Particles in Colloidal Suspensions, with Special Reference to Perrin's Investigations.* *By* Alfred W. Porter, *D.Sc., F.R.S., F.Inst.P., President of the Faraday Society, and* J. J. Hedges, *B.Sc.* *

In the Proceedings of the Royal Society for January last (A. vol. 100, No. 705) E. F. Burton criticises Perrin's work on the law of distribution of particles in colloidal solutions. In the course of his work Perrin shows that, at any rate when the solution is dilute, we should expect a law of distribution of the particles analogous to that which characterises the distribution of the molecules in an atmosphere. By balancing the osmotic pressure of the particles against the effect of gravity he deduces the equation

$$\frac{RT}{N}\log_e \frac{n}{n_0} = V(\rho_1-\rho_2)g(h-h_0),$$

where n and n_0 are the numbers of particles present per unit volume (*i.e.*, the *numerical concentration*) at depths h and h_0, V is the volume of each particle, ρ_1 and ρ_2 the densities of the material of the particles and of the medium respectively. Experimentally, for example, Perrin obtains for particles of gamboge, $2{\cdot}12\times10^{-5}$ cm. diameter, the number of particles at four depths differing successively by 3×10^{-3} cm. and finds values proportional to the numbers 12, 22·6, 47, and 100, which numbers are almost in the same proportion as the members of the geometric progression 11·1, 23, 48, 100. Burton's criticism amounts to saying that if this law of doubling continued as the depth increases then at 3 cms. depth the concentration should become 2^{1000} times the first value given (viz., 12). Now this ratio is a number containing more than 300 digits; and even casual observation shows that no such increase occurs. In fact, Burton makes experiments to show that throughout most of a tall column of suspensoid there is no sensible change in the concentration.

Perrin's own observations were confined to very small ranges near the top of the suspensoid where the concentration was very small, in order that his theoretical and experimental work might correspond to one another. He says in "Les Atômes," § 61, "Ce n'est pas sur une hauteur de quelques centimètres ou même de quelques millimètres, mais sur des

* Communicated by the Authors. A paper read before the Faraday Society, Monday, June 26th, 1922.

hauteurs inférieures au dixième de millimètre, que l'on peut étudier utilement les émulsions que j'ai employées."

We have thought it important not only to prove that the concentration tends to uniformity as the depth increases, but also to find the law of change when the concentration ceases to be sufficiently dilute for the perfect gas equations to hold good.

Experimental.

A suspension of gamboge was prepared by rubbing the solid under distilled water with a soft brush. From this, one in which the particles were practically of the same size was obtained by means of fractional centrifuging. The process actually adopted was that worked out and described by E. Talbot Paris *.

To count the number of particles at various depths, a modified arrangement of the Zeiss ultra-microscope was used. The cell in which the suspensoid was contained was viewed by the microscope placed with its axis horizontal, while it was illuminated by a vertical beam passing downwards through the cover slip which served as a lid to the cell. This vertical beam was obtained from the horizontal beam passing from the lantern through the usual lens system by means of suitably placed reflexion prisms.

The final condensing lens with its screw adjustment was placed with its axis vertical, and the cell was attached to and movable with this lens, so that various depths could be examined in turn. An iris diaphragm in the *eyepiece* permitted the field to be cut down until the number of particles visible at any moment was sufficiently small to be estimated at a glance. To diminish convective effects the light was passed through a water-cell, and a shutter was employed so that the light only passed through the observation-cell for a time sufficient to enable the particles to be counted. With the exterior of the cell blackened and all stray light screened off, it was found possible to count the particles in the field of view over a range of several millimetres from the surface. This arrangement was not convenient for making observations so close to the surface as those made by Perrin which were all confined within the range of less than 0·1 mm.; but this was no drawback to the object we had in view.

The method of obtaining the concentration at any depth was to count the number of particles in the field of view from twenty to forty times at intervals of ten seconds, and

* Phil. Mag. xxx., October 1915.

then to take the mean of these counts. The volume to which these counts correspond is governed by the diameter of the circular field and by the depth of focus of the objective, both of which were determined: its value was $2{\cdot}1 \times 10^{-7}$ cm.^{3}. The depths were measured (by means of the micrometer screw which moved the cell) from an arbitrary level, which was found to be about ·023 cm. from the surface. The depth reckoned from the surface we denote by y, the number of particles per unit volume (*i. e.*, the numerical concentration) by n.

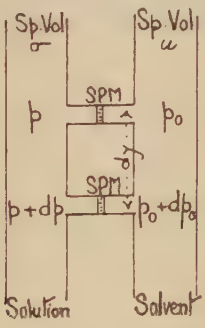
Several complete sets of observations were taken in order to practice the method. The results for the final sets are given below :—

y.	·023.	·033.	·043.	·063.	·083.	·103.	·123.	·143.
Number of counts	·20	20	20	20	40	20	20	40
Total number of particles counted	4	9	15	30	72	40	41	82
Number per count	·20	·45	·75	1·50	1·825	2·00	2·05	2·05
$n \times 10^{-6}$	·95	2·14	3·61	7·14	8·69	9·52	9·76	9·76

Professor Perrin's calculations are explicitly based upon the assumption of the application of the laws of perfect gases to dilute solutions.

It is easy formally to extend them to solutions of any concentration. This was done by one of us for true solutions in 1917 *.

Fig. 1.



Imagine a column of solution to be put into connexion with a column of pure solvent at two points through semi-permeable membranes, the difference of depths of these points

* Porter, Faraday Society. Discussion on Osmostic Pressure, 1917.

being dy (reckoned positive when downwards). The concentration of the solution at any depth is c where $c=nm$, m the mass of a particle and n the number of particles per c.c. (*i. e.*, the numerical concentration). Considering the osmotic pressure P, *i. e.* $p-p_0$, as being a function both of the hydrostatic pressure of the solution, p, and of the numerical concentration, we have the mathematical identity

$$\frac{d\mathrm{P}}{dp}=\left(\frac{\partial \mathrm{P}}{\partial p}\right)_n+\left(\frac{\partial \mathrm{P}}{\partial n}\right)_p\cdot\frac{dn}{dy}\cdot\frac{dy}{dp}.$$

Now $\dfrac{\partial \mathrm{P}}{\partial p}=\dfrac{u-s}{u}$, where s is the shrinkage*, and simple hydrostatic considerations give $\dfrac{d\mathrm{P}}{dp}=1-\dfrac{dp_0}{dp}=\dfrac{u-\sigma}{u}$; also $\dfrac{dp}{dy}=\dfrac{g}{\sigma}$.

Therefore
$$\frac{s-\sigma}{u}=\frac{\sigma}{g}\cdot\frac{\partial \mathrm{P}}{\partial n}\cdot\frac{dn}{dy}.$$

This formula is exact, and is independent of any particular hypothesis of the mechanism of the variation.

Now it was shown by Sackur and by one of us that the variation of P with concentration in the case of a sugar solution can be represented very nearly, up to high concentrations, by the formula

$$\mathrm{P}=\frac{nr\mathrm{T}}{(1-bn)},$$

where b is a constant which is of the same order of size as, but is larger than, a molecule of sugar. If we assume the applicability of the same type of formula to a suspension of gamboge

$$\frac{\partial \mathrm{P}}{\partial n}=\frac{r\mathrm{T}}{(1-bn)^2}.$$

In these formulæ r, which applies to an actual particle, is connected with the usual molecular gas constant, R_0 (which refers to one gram-molecule), by the equation

$$r=\frac{\mathrm{R}_0}{\mathrm{N}},\ \text{where N is Avogadro's number.}$$

Hence
$$\frac{dn}{dy}=\frac{s-\sigma}{u\sigma}\cdot\frac{g\mathrm{N}}{\mathrm{R}_0\mathrm{T}}(1-bn)^2.$$

* Porter, Proc. Roy. Soc., A. 1907, p. 522.

If we assume that there is no contraction when gamboge and water are intermingled

$$\sigma = c\gamma + (1-c)u \text{ and } s = u,$$

where γ = density of solid gamboge. Hence

$$\sigma - s = c(\gamma - u) = nm(\gamma - u).$$

Further writing $$K = \frac{\sigma N m(u-\gamma)}{R_0 T u^2}$$

and, putting σ in denominator as equal to u [which is justifiable, because even the strongest suspensions of gamboge are fairly dilute],

$$\frac{dn}{dy} = Kn(1-bn)^2.$$

The integral of this equation is

$$\log_e \frac{n}{1-bn} + \frac{1}{1-bn} = K\gamma + A,$$

where A is the constant of integration which can be expressed in terms of (the unknown) concentration when $\gamma = 0$. This is a curve which tends asymptotically for large values of γ to the value $n_\infty = 1/b$; and which has a point of inflexion for $n = n_\infty/3$.

A curve of this kind can be fitted to the experimental curve within the limits of experimental accuracy (fig. 2).

The following values are obtained by taking

$$b = 10{\cdot}2 \times 10^{-8} \text{ cm.}^3 \text{ and } K = 121 :—$$

y (in cms.).....	·024	·032	·0375	·047	·061	·089	·115
$n \times 10^{-6}$	1	2	3	5	7	9	9·7

A closer fit could, of course, be obtained by allowing b to vary with the concentration, as was done in examining the osmotic pressure of sugar solutions *. It is difficult, however, in the present problem, to give anything but an empirical significance to this constant. It enters into the osmotic pressure in the same way as the least volume of the liquid enters into the gas equation. But in this case it would mean that even in the fairly dilute concentrated suspension of gamboge the effective volume of the particles is the volume of the solution itself—that is to say, that the suspensoid

* Porter, *loc. cit.*

plus the atmosphere (or ocean) of solvent (or second phase) which surrounded it, and to which it was attached (so that motion of one entailed similar motion of the other), constituted the whole of the substance present. The radius calculated by considering b as the effective volume is 28×10^{-4} cm. Now it is hard to think that the whole of the liquid in the domain of a particle should be so attached to the particle as to form practically part of it, for, if this were so, the whole suspension would be rigid. It might be conceivable in the case of even a dilute concentration of gelatine, for this can form a rigid gel; no such rigidity is observed in the case of gamboge. It is noteworthy, however, that if b be regarded as an effective volume, then b and K are not independent constants, for K is proportional to the effective volume of the particle. When the radius is calculated from K, it is found to be $1{\cdot}6\times10^{-5}$ cm., which is very much less than when calculated from b, but is certainly a measure of the effective radius of the particles that were examined. We return to this point later.

It is safer, however, to regard b as merely an empirical constant. It may be pointed out that Callendar's equation for unsaturated steam is of the form

$$p(v-b)=\mathrm{RT},$$

where, however, b is even negative and represents the combined effects arising from the finite size of the molecules and the *attractive* forces which tend to "co-aggregate" the molecules. It is noteworthy, however, that, if b is to become large and remain positive, *repulsive* forces are required.

Burton, in the second edition of his monograph on the physical properties of colloidal solutions, page 87, attempts to explain the present problem by considering repulsion arising from the electrical charges in the particles. He concludes that the forces on any layer due to the rest of the solution will be of the form kne per unit charge on the layer dh, where k, he considers, may be taken as a constant, *at any rate for regions near the surface*, and e is the charge in electrostatic units on each particle. Consequently the total force per unit area is kn^2e^2dh. A term of this kind is taken to represent the excess electrical repulsion of all the particles below dh over that due to those above dh. Perrin's equation then becomes, for the forces balancing per unit area,

$$\frac{\mathrm{RT}}{\mathrm{N}}dn+kn^2e^2dh=n\mathrm{V}(d-w)gdh.$$

Writing this in the form $A\,dn = n(C - Bn)\,dh$, and solving, he gets

$$n = \frac{C}{B + Ke^{-ChA}},$$

in which $K = (C - Bn_0)/n_0$ and n_0 is the concentration when $h = 0$. To obtain Perrin's formula B must be put equal to zero. The ratio C/A can therefore be obtained from Perrin's experiments. Calculation shows that e^{-ChA} tends rapidly to zero as h increases, and ultimately n becomes

$$n_\infty = \frac{C}{B} = \frac{V(d-w)g}{ke^2}.$$

The depth at which this uniform concentration is practically attained will depend upon the relative values of K and B; it will be nearer the surface the larger the electrical forces are compared with the gravitational.

Now there are serious objections to the theory as thus stated.

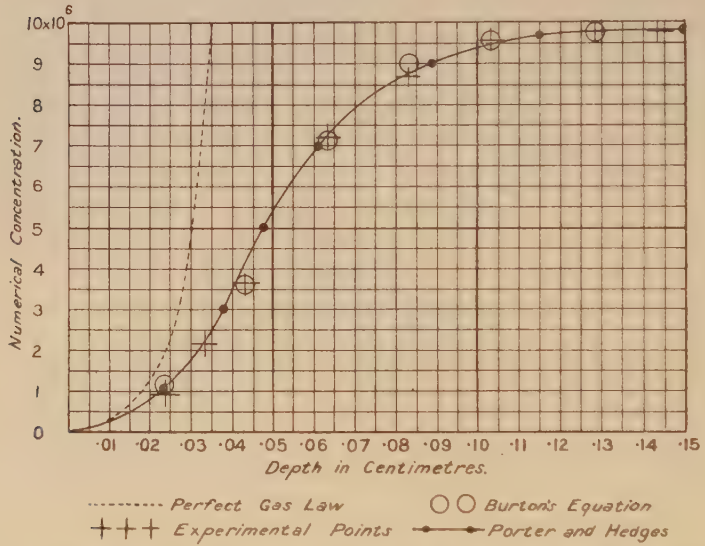
In the first place, if the particles really contained charges all of one sign only they would tend to move toward the boundary. This is the equivalent of the fundamental electrical fact that statical charges reside close to the surface of conductors. When we are dealing with large particles instead of electrons, there is no doubt that they would occupy a larger region, instead of a thin superficial area, but still there would be an accumulation at the boundary. This is the opposite to what is observed.

But the charges in the solution are not only of one sign. The solution, as a whole, is uncharged; consequently an equal opposite charge is to be looked for. This opposite charge is the second member of the double layer close to the surface of each particle. When the existence of this double layer is recognized, the electric forces between the particles become zero, except in so far as relative displacement takes place by induction between two members of a layer so as to give it an electrical movement. In this case the force between two such doublets in the equilibrium state will, on the average, be an *attraction* and not a repulsion.

Now we have fitted a curve calculated from Burton's equation to the experimental points. They are shown by large circles on the figure and are seen to fit the experiments remarkably well. In view of the above objections to the

theory, this cannot be taken as indicating more than that in the differential equation for the distribution there is a term proportional to n^2 in addition to the one depending on n.

Fig. 2.



From the form which Burton gives to his force term there appears to be some confusion in his mind between force and pressure. If his statements were to be taken as correct, there would be a uniform *force* on any layer (counteracting the uniform force of gravity) in the greater part of the solution, for his force term is proportional to n^2 and n becomes practically uniform ; whereas it is clear that in the middle where a layer would be driven as much up as down the force would really vanish.

Now, although b in a van der Waals' formula represents the volume of a particle when it is treated as a rigid body, it is in general the coefficient of the internal virial arising from molecular repulsions during "collisions." The large value obtained with gamboge would indicate therefore that, even when particles are at a distance from one another much greater than that which denotes their size when it is estimated by optical examination with a microscope, the particles begin to experience a mutual repulsion. To put it in other words, the actual visible particle is connected in a semi-rigid way with a very large quantity of the surrounding fluid. What the nature of this connexion may be can only be a matter

for speculation. A sugar molecule is tied in a more or less rigid way with at most a single layer of water molecules *. Molecules, however, attract one another with forces which vary according to a high power of their distance apart. But the very large particles of gamboge have a far greater range of action. Large masses attract according to the law of gravitation. The particles in question may be assumed to attract molecules of water with a force varying according to some intermediate law, and have in consequence an intermediate range of action. Thus they can form a loose combination with comparatively large masses of water, each such agregate moving as a single molecule, so far as kinetic theory is concerned. Hence the large value of b, which is determined by the mean radius at which such units bounce off one another.

Nothing that is said here must be taken as excluding the action of other intermolecular forces besides those concerned with collisions. If analogy with a van der Waals' substance is made use of, the osmotic pressure could be written

$$p + an^2 = nr\mathrm{T}/(1-bn),$$

where it may be left an open question as to whether a is positive (attraction) or negative (repulsion).

The equation for dn/dy then becomes

$$\frac{dn}{dy}\left\{\frac{1}{n(1-bn)^2} - \frac{2a}{r\mathrm{T}}\right\} = \mathrm{K};$$

whence

$$\log\frac{n}{1-bn} + \frac{1}{1-bn} - \frac{2an}{r\mathrm{T}} = \mathrm{K}y + \mathrm{A}.$$

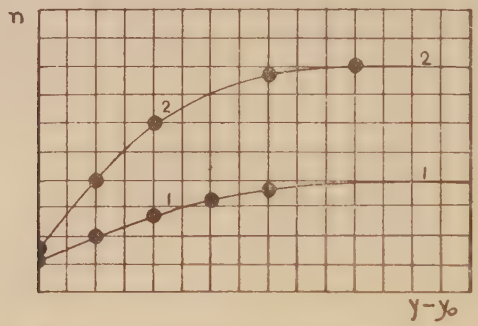
The limiting volume of n is still determined, not by a, but by b, and this is so whether a is positive or negative.

Further light is thrown upon the phenomenon by taking suspensions of various limiting concentrations. In fig. 3 are shown experimental curves for two cases; in curve 2 the limiting concentration (*i. e.*, the concentration in all except the upper layers) is twice the value for curve 1. Hence, according to the equation given, the value of b in the latter (*i. e.*, the dilute solution) is twice the value it has for the stronger solution. This, again, is quite in accordance with the behaviour of sugar, for which substance more molecules of water were found to be attached to each molecule of sugar in the case of a dilute solution than in the case of a strong one.

* Porter, *loc. cit.*

These last experiments show that care should be taken to avoid thinking of the limiting concentration as necessarily giving a *saturation* value. The same kind of curve is obtained when more dilute suspensions are investigated. The value of K is also different for the two curves. For curve 1 (fig. 3) it is about 29, while for curve 2 it is 55. It would seem that the size of the solid nucleus diminishes to one-half when the suspension is reduced to half strength.

Fig. 3.

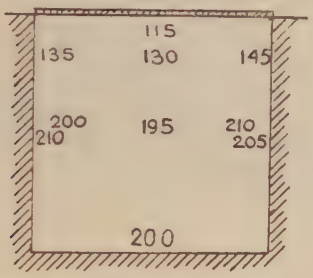


Although Burton's particular assumption of the existence of an electrical repulsion between the particles has been here criticised, it might still seem an open question as to whether some other force between them might not be the operative cause. The chief difficulty applicable to all possible laws of force is that such forces will be exerted in all directions and must act outwards at every surface. Hence, though near the top of the fluid they might be assumed of such a character as to oppose gravitation, at the bottom they should assist it in producing a change of concentration, which might be expected to be exceedingly large in consequence. Again, at the sides where the forces would act laterally they would produce a change of concentration independent of gravitation. What really happens can be seen from fig. 4, which represents the approximate relative values of the numerical concentrations actually observed at various points of a cell $\frac{1}{2}$ cm. deep and $\frac{1}{2}$ cm. broad. It is obvious from the numbers given in the figure that the only variation of concentration is near the top. It ought to be mentioned that, since the suspension was covered with a microscope cover-glass, the suspension was surrounded by glass on all sides; the peculiar effect at the top is therefore not due to a transition from liquid to air.

It would appear from these preliminary determinations that there are in reality three regions in a suspension to-

which particular names might be given. In the first place, there is a very thin layer close to any surface in which there may be a special value for the mean concentration. This is the layer discussed by Willard Gibbs, and has been called after him. Its thickness is of the order of the range of

Fig. 4.



intermolecular forces. Secondly, there is the layer studied by Perrin, "inférieure au dixième de millimètre," in which the change of concentration of a suspensoid can be calculated from an application of the laws of gases in an analogous way to that in which the change of pressure of an atmosphere is calculated. This is the Perrin layer. Thirdly, there is a layer of one or two millimetres' thickness (in the particular cases studied in this paper), in which a further change of concentration occurs which cannot be calculated in the way adopted by Perrin. This gradually merges into the main body of the suspension, throughout which the concentration is sensibly uniform.

LVII. *On the Emission Spectrum of Monatomic Iodine Vapour.* *By* St. Landau-Ziemecki, *M.Sc., Lecturer in Physics, High School of Agriculture, Warsaw* *.

I. *The aim of this work.*

MANY of the phenomena of the multiple spectra were ascribed to the dissociation of the molecules or even of the atoms (the work of Lockyer may be only mentioned), but there does not seem to be *direct experimental* evidence for such a theory. On the other hand, the models of atoms and molecules, now generally adopted, lead us to the idea that an atom should give a spectrum quite different from the

* Communicated by the Author.

Presented to the Polish Academy of Sciences by Prof. L. Natanson, March 7th, 1921, and published in the *Bulletin de l'Académie Polonaise*, série A, 1921. Since that time the experiments have been verified by the Author.

spectrum of the molecule. To verify it experimentally the writer chose iodine, the dissociation of which has been well studied and which dissociates at a relatively low temperature.

II. *The Experiments.*

Bodenstein and Starck * have shown that the dissociation equilibrium can be expressed by the formulæ :

$$\frac{p_1^2}{p_2} = K\,;\quad \log K = -\frac{7762}{T} + 1{\cdot}75 \log T - 0{\cdot}000416\,T + 0{\cdot}422,$$

where p_1 is the pressure of the monatomic iodine vapour, p_2 the pressure of the diatomic vapour, K the equilibrium constant, T the absolute temperature. This expression agrees well with the experiments. Applying that formula, we obtain the following table for the degree of dissociation—that is, the ratio of dissociated molecules to the total number of the molecules which would be present were there not any dissociation.

Degree of dissociation as a function of pressure and temperature.

	t=500°C.	600°.	700°.	800°.	900°.	960°.
$p=\frac{1}{4}$mm.	0·1	0·36	0·76	0·95	0·99	1
$p=1$ „	0·05	0·19	0·52	0·83	0·94	1
$p=10$ „	0·02	0·06	0·19	0·42	0·68	0·81

Taking these data as the starting point for my experiments, I prepared a Geissler tube from quartz of the form shown in fig. 1 †.

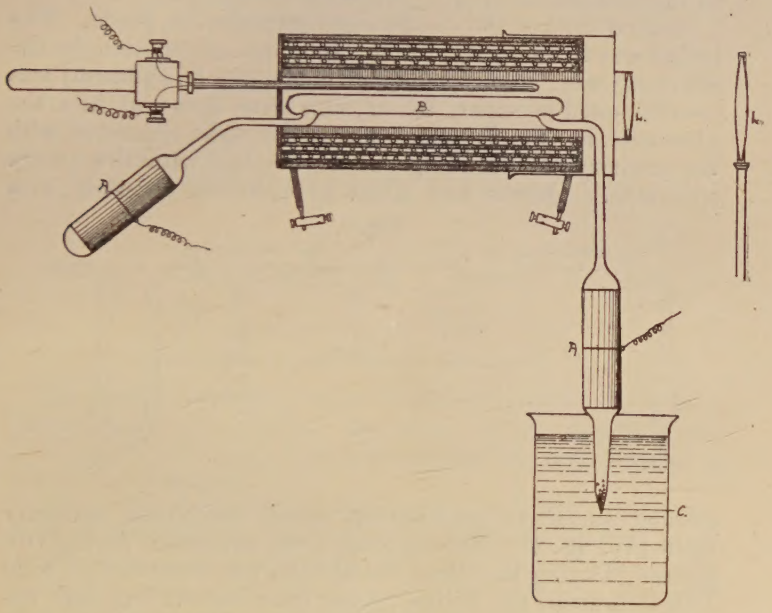
The iodine crystals were at C, and that part of the tube was immersed in a water-bath, the temperature of which varied in the different experiments from 15°–20° C.; thus the corresponding vapour-pressure was always less than 0·25 mm. of mercury (for 20° C.). The central part of the Geissler tube was placed in an electric oven, and the temperature raised from 960°–1000° C. It is seen from the above table that in these conditions the dissociation was fairly complete.

* *Zeitschrift für Elektrochemie*, vol. xvi. p. 961 (1910).

† Some months after this work was published in the Bulletin of the Pol. Acad., W. Steubing described in the *Physikalische Zeitschr.* (1921, p. 507) his experiments touching the influence of the temperature on the band spectrum of iodine. The experimental arrangement of this author was similar to mine. Glass tubes were used by him, and thus he was unable to go further than 450° C., when practically there is no possibility of observing any trace of the line spectrum of monatomic iodine, the percentage of dissociated molecules being quite insignificant. The experiments of W. Steubing gave interesting results touching the weakening of the band spectrum with the rise of the temperature. His observations are limited to the visible part of the spectrum. This part of the spectrum was inaccessible to me in the experiments touching the spectrum of monatomic iodine on account of the radiation of the electric oven.

It is obvious that in the case considered there exists a circulation of the vapour, but, for the diameter of the joining quartz tubes, no serious pressure differences could exist; besides, it was shown by Nernst * and his collaborators that the dissociation formulæ can be applied to a gas flowing through a pipe, if the flow is not too quick a one.

Fig. 1.



Two main iodine spectra are known—a band spectrum and a line spectrum. The most complete study of these spectra was made by H. Konen †. Condensed, strong discharges in narrow parts of the Geissler tubes give generally the line spectrum; with wide tubes and feeble discharges we obtain the band spectrum. The first experiments to show the influence of the dissociation on the emission spectrum were made by the author, using Geissler tubes of ordinary shape with vertical capillary tube. No interesting results were obtained. A new spectrum was observed when using a tube "end on" with large central part, as is seen in fig. 1; the central part B had a length of about 12 cm. and a diameter of 1 cm.; the parts A, covered with tinfoil, had a diameter of about 3 cm. and a length of about 8 cm. This tube, not

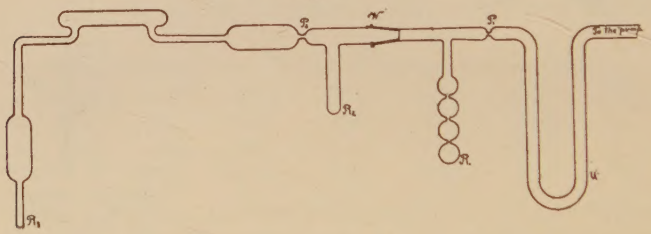
* W. Nernst, *Theoretische Chemie*, 7th ed. p. 709. W. Nernst and H. v. Wartenberg, *Zeitschrift f. physik. Chemie*, vol. lvi. p. 535 (1906).

† *Annalen der Physik*, vol. lxv. p. 265 (1898).

heated, showed the ordinary band spectrum. The temperature being raised to 960°–1000° C., the conditions of the electric excitation remaining the same, a new line spectrum replaced the band spectrum. The appearance of that spectrum is quite different from the appearance of the spectrum obtained in a narrow tube with condensed discharges. It consists of relatively few lines; two lines in the ultra-violet are especially strong and characteristic; the others are faint.

Some details of the experiments may now be given. The iodine was introduced into the tube by sublimation in the following way. Pure iodine of commerce (Kahlbaum) was re-sublimated *in vacuo*; the crystals were then put into the glass tube R_1 (fig. 2), which was to the right connected with the mercury Gaede pump and to the left with the quartz apparatus. Quartz and glass were joined together with

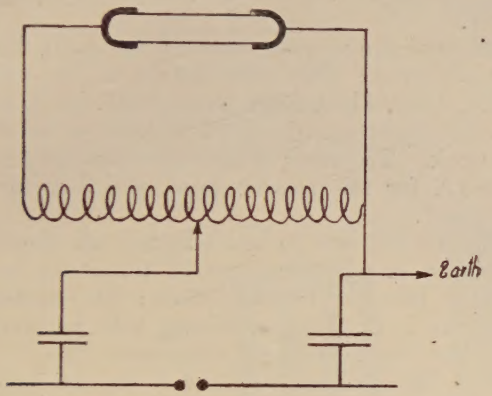
Fig. 2.



ground surfaces; sealing-wax made that joint perfectly tight (W, fig. 2). The apparatus was exhausted during two hours. During that time the U-tube was immersed in solid CO_2 to prevent the iodine vapour from penetrating into the pump; at the same time the quartz part of the apparatus, which was previously chemically cleaned, was now heated in the most energetic manner with a Bunsen burner and finally with a blow-pipe. The apparatus was then cut away from the pump at P_1, and the iodine sublimated from R_1 to R_2, this part being immersed in liquid air. After some hours, R_3 was in turn immersed in liquid air, and a crust of iodine crystals was formed there. Every precaution against contamination having been taken, the quartz part of the apparatus was again put in communication with the pump, and after an exhaustion of half-an-hour's duration the quartz apparatus with the iodine crystals at R_3 was cut away from the pump at P_2. The Geissler tube obtained was put in the electric oven shown in fig. 1, and finally bent with the coal-gas oxygen flame in the desired manner. The tube was provided with external electrodes formed by tinfoil cemented to the quartz with a mixture of graphite powder and water.

The luminescence of the tube was excited either by connecting it directly with the secondary of a Ruhmkorff induction coil (15 cm. spark), or by using in connexion with the induction coil a high-frequency transformer of the Oudin type, and joining the tube to the circuit as shown schematically in fig. 3; in the latter case a Wehnelt interruptor was used.

Fig. 3.



The temperature of the electric oven was measured with a thermo-couple Pt—Pt/Rh. By means of two quartz lenses (L in fig. 1) the light was concentrated on the slides of a quartz spectrograph.

At low temperatures the tube has shown a band spectrum. H. Konen * finds that the band spectrum is almost continuous in the ultra-violet part, having only few diffused maxima at $\lambda=3300$, 4270, 4520, 4760 Å. On the contrary, I found that this band spectrum has a very regular structure with many well-defined maxima. There seems to be no discrepancy between our results: this author has taken photographs with long exposures, and in these circumstances, as I find, all details disappear; on the contrary, my exposures never lasted longer than a few minutes. For a more detailed study of the band spectrum, I used a special quartz tube with external electrodes, having a capillary part in the middle. This tube being connected with the secondary of a Ruhmkorff coil, I found distinct maxima at $\lambda=422$, 404, 395, 387, 380, 373, 368, 363, 340, 325, 323, 320, 319, 312, 310, 306, 304, 302, 299 $\mu\mu$; for shorter wave-lengths the maxima were too feeble to be measured.

Raising the temperature of the oven, I found that the transformation of the band spectrum into a line spectrum occurred gradually. At 550° C. we have yet a band spectrum;

* *Loc. cit.*

at 650° C. one of the two characteristic lines 3281 Å appeared; the second strong line 3384 Å appeared later; at 800° C. it was yet faint. The manner of producing the spectra seemed to be of no influence: I observed the same phenomena whether applying uncondensed discharges of a Ruhmkorff coil provided with the hammer interruptor, or with the Oudin high-frequency transformer, acuated by an electrolytic interruptor.

I determined the wave-lengths of the main lines of the spectrum observed; they were found to be 4868, 4769, 4680, 4324, 4132, 4100, **3384**, **3281**, 3081, 2879, 2593, 2583, 2566 Å. My spectrograph had a dispersion insufficient for accurate work. The error of the determinations should not exceed 2–3 Å for the fainter lines, and 1 Å for the two stronger ones*.

It would be difficult to tell whether all these lines are absolutely new, or whether some of them can be found in the ordinary line spectrum of iodine: the exactness of my measurements is insufficient, taking into account that the lines of iodine are exceedingly numerous; happily there are no lines of the ordinary spectrum in the proximity of 3281 Å; that characteristic line is thus certainly a new one.

III. *Results.*

A new line spectrum of iodine was observed, and wave-lengths of the main lines approximately determined. This spectrum belongs evidently to the atom of iodine; it appeared more and more distinctly with increase of the dissociation of iodine molecules; at the same time the band spectrum disappeared. The band spectrum of iodine seems thus to be inherent in the molecule. It was found that the band spectrum possessed in the ultra-violet a very regular structure, contrary to that which had hitherto been imagined.

It may be permitted to the Author to express here his best thanks to Prof. S. Pienkowski, who in a most generous way has supplied him with a quartz spectrograph.

A great part of the expense was covered by the Mianowski Foundation.

Warsaw, Physical Laboratory of the
State Technical School, founded
by H. Wawelberg and S. Rotwand.
May 1922.

* In the violet part of the spectrum much greater errors are possible, the dispersion of the quartz prisms being there very small. While this paper was in the press some other lines were measured and the following wave-lengths found: 4640, 4414, 4217, 3576. 2528, 2524, 2516, 2507.